

CHARACTERIZATION OF NOVEL PATHWAYS IN THE PHOSPHORUS CYCLE OF LAKES

A Thesis Submitted to the College of
Graduate Studies and Research
In Partial Fulfillment of the Requirements
For the Degree of Doctor of Philosophy
In the Department of Biology
University of Saskatchewan
Saskatoon

By

Jeffrey Michael Sereda

© Copyright Jeffrey Michael Sereda, March, 2011. All rights reserved.

PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a postgraduate degree from the University of Saskatchewan, I agree that the Libraries of this University may make it freely available for inspection. I further agree that permission for copying of this thesis in any manner, in whole or in part, for scholarly purposes may be granted by the professor or professors who supervised my thesis work or, in their absence, by the Head of the Department or the Dean of the College in which my thesis work was done. It is understood that any copying or publication or use of this thesis or parts thereof for financial gain shall not be allowed without my written permission. It is also understood that due recognition shall be given to me and to the University of Saskatchewan in any scholarly use which may be made of any material in my thesis. Requests for permission to copy or to make other use of material in this thesis in whole or part should be addressed to:

Head of the Department of Biology
112 Science Place
University of Saskatchewan
Saskatoon, Saskatchewan S7N 5E2

ABSTRACT

Phosphorus (P) is a limiting nutrient regulating productivity in both freshwater and marine ecosystems. A full knowledge of the sources and pathways of the P cycle is essential for understanding aquatic ecosystem function and for managing eutrophication. However, two significant pathways are poorly understood or remain uncharacterized. First, aquatic metazoans represent a significant internal regenerative pathway of P through the mineralization, translocation (i.e., benthic pelagic coupling) and excretion of nutrients. Rates of P excreted are expected to vary across taxa (i.e., zooplankton vs. mussels vs. benthic macroinvertebrates vs. fish), yet the significance of any one group of taxa in supplying P to bacteria and algae is unknown. Therefore, I developed the first comprehensive set of empirical models of nutrient release for aquatic metazoans (zooplankton, mussels, “other” benthic macroinvertebrates, and detritivorous and non-detritivorous fish) and compared inter-taxonomic differences in P excretion. I demonstrated that detritivorous fish excrete P at rates greater than all other taxa (as a function of individual organism mass); whereas, mussels generally excreted P at rates less than other taxa. Significant differences in the rate of P excretion between zooplankton and non-detritivorous fish were not observed [i.e., the allometry of P excretion was similar between zooplankton and non-detritivorous fish (as a function of individual body mass)]. I subsequently applied the models to assemblage biomass and abundance data to examine and compare the relative contribution of each taxa to the internal supply of P, and to examine the turnover time of P bound in metazoan biomass. I clearly demonstrated a hierarchy in the contribution by different metazoan assemblages to P cycling (zooplankton > benthic macroinvertebrates > mussels > fish) and clarified

the significance of different metazoan taxa in P cycling. Moreover, I demonstrated that the slow turnover time of P bound in fish biomass (relative to other metazoans) indicates that fish are important as sinks rather than sources of P.

A second potentially significant P pathway is through the influence of ultraviolet radiation (UVR) on P cycling. UVR may alter P cycling abiotically through changes in P availability and biotically through changes in the acquisition and regeneration of dissolved P by plankton. However, the significance of P released from the photodecomposition of dissolved organic P compounds (DOP), and the effect of UVR on the uptake and regeneration of dissolved P, the turnover of particulate P, and on ambient phosphate (PO_4^{3-}) concentration has not been investigated and remains unknown.

Therefore, my initial experiments applied the novel use of radiophosphate uptake assays to quantify the significance of the photodecomposition of DOP to PO_4^{3-} . I concluded that the liberation of PO_4^{3-} through the photodecomposition of DOP is not a significant pathway. However, the photochemical liberation of PO_4^{3-} from suspended sediments was evident and should be an important pathway supplying PO_4^{3-} to plankton in shallow polymictic lakes. This represents the first study to identify this P pathway in lakes.

The turnover time of the PO_4^{3-} pool increased under UVR irradiance (i.e., uptake of P by plankton decreased), while the regeneration rate of dissolved P and turnover rate of planktonic P were generally not affected. The net effect of UVR was an increase in steady state PO_4^{3-} concentration (ssPO_4^{3-}). Alkaline phosphatase activity (APA) in the dissolved and particulate fractions was significantly reduced in UVR treatments, but unrelated to changes in P uptake as proposed in the literature. This is the first study to

comprehensively investigate the biotic effects of UVR on P cycling and represents a major advancement in the field of photobiology.

In summary, I have characterized several poorly understood pathways in the P cycle of lakes. With the models I have developed, aquatic metazoans can now be integrated into the P cycle of lakes, for example, with other internal and external sources of P (e.g., from inlets, lake sediments and the atmosphere). This will advance our knowledge of P cycling, and will provide researchers with a better understanding of the nutrient pathways supporting primary production.

ACKNOWLEDGEMENTS

First and foremost, I would like to thank my wife, Lorilee Sereda, for the moral and emotional support during my many long hours in the field, in the laboratory, and in my office writing. I would also like to thank both my mom and dad for instilling in me a passion for the outdoors and a strong work ethic. Both of which were essential for my success in obtaining this degree. I owe thanks to my Supervisor, Jeff Hudson, and my committee members, Som Niyogi, Dick Neal, and John-Mark Davies. These individuals provided the professional direction and expertise required to allow me to complete my Doctoral program. I am grateful for the additional support provided by David Vandergucht. This individual was my lab mate and friend and provided me with support in the field and laboratory. I would also like to thank Jeff Hudson, David Vandergucht and W.D. Taylor for the many valuable comments, suggestions and insightful discussions that improved and directed my research. I would like to thank Roger Bachmann, Charles Ramcharan and Norman Yan for generously providing data essential to my study. Finally special thanks to the Dorset Environmental Science Centre for providing assistance, laboratory space, and equipment. Finally, I would like to thank the University of Saskatchewan, Saskatchewan Environment and Resource Management, and the Malcolm A. Ramsay Memorial Award for providing financial support.

Table of Contents

Permission to Use.....	i
Abstract.....	ii
Acknowledgements.....	v
Table of Contents.....	vi
List of Figures.....	ix
List of Tables.....	xiii
Chapter 1: Phosphorus in Limnetic Systems.....	1
1.1. Introduction.....	1
1.2. Mass Balance Models.....	4
1.3. Frequently Measured Sources of Phosphorus.....	5
1.3.1. Groundwater.....	5
1.3.2. Atmospheric.....	5
1.3.3. Internal Loading.....	6
1.3.4. Tributaries.....	6
1.4. Infrequently Measured or Un-quantified Sources of Phosphorus.....	7
1.4.1. Fish.....	7
1.4.2. Macroinvertebrates.....	7
1.4.3. Abiotic Effects of Ultraviolet Radiation.....	8
1.4.4. Biotic Effects of Ultraviolet Radiation.....	9
1.5. Objectives.....	9
Chapter 2: General Empirical Models for Predicting the Release of Nutrients by Fish...	11
2.1. Introduction.....	11

2.2. Methods.....	13
2.3. Results.....	22
2.4. Discussion.....	30
Chapter 3: General Empirical Models for Predicting the Release of Nutrients by Aquatic Metazoans.....	36
3.1. Introduction.....	36
3.2. Methods.....	38
3.3. Results.....	43
3.4. Discussion.....	58
Chapter 4.1: Fish as Sources and Sinks of Phosphorus.....	67
4.1.1. Introduction.....	67
4.1.2. Methods.....	69
4.1.3. Results.....	75
4.1.4. Discussion.....	84
4.2. The Significance of Fish Carcasses in Phosphorus cycling.....	95
Chapter 5: Effects of Ultraviolet Radiation on Phosphorus Kinetics.....	101
5.1. Abiotic Effects.....	101
5.1.1. Introduction.....	101
5.1.2. Methods.....	103
5.1.3. Results.....	109
5.1.4. Discussion.....	113
5.2. Generality of the Response of Dissolved Organic Phosphorus to Ultraviolet Radiation.....	117
5.2.1. Introduction.....	117

5.2.2. Methods.....	117
5.2.3. Results.....	118
5.2.4. Discussion.....	123
5.3. Biotic Effects.....	125
5.3.1. Introduction.....	125
5.3.2. Methods.....	127
5.3.3. Results.....	137
5.3.4. Discussion.....	146
Chapter 6: Synthesis and General Conclusions.....	151
6.1. Significance of Aquatic Metazoans.....	151
6.2. Effects of Ultraviolet Radiation on Phosphorus Kinetics.....	154
6.2.1. Abiotic Effects.....	154
6.2.2. Biotic Effects.....	155
6.3. Summary.....	155
Literature Cited.....	157
Appendix 3.1.....	181
Publications and Conference Presentations.....	187

List of Figures

Figure 1.1. Diagram of the primary P pathways in lakes. Pathways in bold with dotted arrows signify pathways that have not been quantified or their significance to the overall nutrient budget are poorly understood.....	3
Figure 2.1. The release of nutrients ($\mu\text{g h}^{-1}$ of N or P) by detritivores and non-detritivores as a function of fish wet mass ($\log(\text{mass (g)})$ or $\log(\text{mass}+1 \text{ (g)})$ and water temperature ($^{\circ}\text{C}$). Note that fish mass is a better predictor of nutrient release than water temperature. Figures were produced with smoothed data, LOESS function, SigmaPlot v. 9. (Systat Software, Inc., Chicago, IL.).....	24
Figure 2.2. Predicted release rates of P ($\text{g ha}^{-1} \text{ d}^{-1}$) ($n = 57$) in relation to total fish biomass (kg ha^{-1}), compared with rates for other lakes obtained from Griffiths (2006) ($n = 18$). Regressions (± 1 standard error of model regression coefficients) are shown for our predicted release rates. Error regressions should be conservative estimates as it is unlikely that the true values will vary in the same direction and magnitude. Slopes and intercepts are not significantly different between the two relationships (t-test, $p > 0.05$). Data were not available to make a similar comparison for nitrogen release.....	27
Figure 2.3. Comparison of N and P release rates when gizzard shad were modeled as 100% planktivores or 100 % detritivores. Fish assemblage data were obtained from Bachmann <i>et al.</i> (1996), and analysis was restricted to the 21 lakes where gizzard shad were present. Gizzard shad accounted for an average of 23% (<1–75%) of total fish biomass in these lakes. Lakes are ordered such that gizzard shad biomass increases from left to right on the x-axis (as a % of total fish biomass). The total quantity of nutrients released increased by an average of 56% (<1–331%) and 62% (<1–211%) for N and P, respectively, when gizzard shad were solely detritivorous. Note that these rates would be representative of average rates if fish had these diets.....	29
Figure 3.1. Rates of nitrogen (a) and phosphorus release (b) ($\mu\text{g h}^{-1}$) and molar N:P ratios predicted by the empirical models (c). Models were applied to the range of organism dry mass (mg) encompassed by each model and to a temperature of 20°C . The Redfield N:P ratio of 16:1 is shown for comparison. Also shown in a) and b) are the slopes (linear regression) for each taxon. Note that detritivorous fish excrete both N and P at rates greater than for other metazoans. Molar ratio of N and P excreted by zooplankton and detritivorous fish decline with increasing organism mass (c) whereas N:P ratios increase with increasing dry mass for all other metazoans. Note that mussel N:P ratios were calculated for Veneroida only.....	51
Figure 3.2. Rates of nitrogen and phosphorus excretion ($\text{g ha}^{-1} \text{ d}^{-1}$) as a function of metazoan biomass (fish, zooplankton and macroinvertebrates) (kg ha^{-1}) in Mouse and Ranger Lakes. Models were applied to the biomass and abundance data in each lake over a 7 year period (1991–1997). Water temperature was held constant at 20°C . Note, that N and P excretion increases linearly with assemblage biomass.....	54

Figure 3.3. Rates of nitrogen (a) and phosphorus (b) excretion ($\text{g ha}^{-1} \text{d}^{-1}$) by aquatic metazoans as a function of assemblage biomass (kg ha^{-1}). Rates were obtained from the literature for marine and freshwater, temperate and tropical systems [fish (Nixon et al. 1976; Horppila 1998; Brabrand et al. 1990; Boers et al. 1991; Schindler et al. 1993; Persson 1997; Gido 2002; Griffiths 2006; Sereda et al. 2008a); benthic macroinvertebrates (Needham 1957; Nixon et al. 1976; Gardner et al. 1981; Madeira et al. 1982; Smith 1983; Gray 1985; Starkel 1985; Grimm 1988; Fukuhara & Yasuda 1989; Nithart et al. 1999; Henry & Santos 2008); zooplankton (Barlow & Bishop 1965; Hargrave & Geen 1968; Jawed 1973; Peters 1975; Bartell 1981; Park & Carpenter 1987; Pinto-Coelho & Greco 1999; Atkinson & Whitehouse 2001; Hernandez-Leon & Ikeda 2005); mussels (Jordan & Valiela 1982; Prosch & McLachlan 1984; Nalepa et al. 1991; Prins & Smaal 1994; Mellina et al. 1995; Ozersky et al. 2009). Regression coefficients for each taxon are presented in Table 1. Note that a regression line is not available for benthic macroinvertebrate P release as only two data points are present. Also note that solid symbols correspond to the same taxa as in the legend, but excretion rates represent mean values of taxon calculated for metazoans in Mouse and Ranger Lakes using our general models.....57

Figure 4.1.1. A) Release of TP by all fish in relation to their wet mass (g), $n = 48$, $R^2 = 0.82$, $p < 0.001$, \log_{10} TP release rate ($\mu\text{g h}^{-1}$) = $0.793(\pm 0.109) [\log_{10} \text{wet mass (g)}] + 0.7817(\pm 0.145)$. Release rates of P across all species ranged from 7.69 to 515.6 $\mu\text{g h}^{-1}$. B) Release of N in the form of NH_4^+ in relation to wet mass (g) for all fish, $n = 46$, $R^2 = 0.88$, $p < 0.001$, \log_{10} N release rate ($\mu\text{g h}^{-1}$) = $0.6946(\pm 0.079) [\log_{10} \text{wet mass (g)}] + 1.7481(\pm 0.108)$. Release rates of N across all species ranged from 72.6 to 2282 $\mu\text{g h}^{-1}$. Confidence intervals (95%) for each regression are shown.....76

Figure 4.1.2. Mean daily release of P and N ($\mu\text{g l}^{-1} \text{d}^{-1}$) by the fish assemblages in Mouse and Ranger Lakes. Confidence intervals (95%) represent cumulative variance of release rates predicted from species specific regressions of nutrient release, C.I. surrounding fish abundance estimates, and variation between daily release rates (July 1 to August 31) of each year.....78

Figure 4.1.3. Comparison of daily release rates of P by the fish assemblage ($\mu\text{g l}^{-1} \text{d}^{-1}$) to regeneration rates of P by the plankton community in Mouse and Ranger Lakes. The 95% C.I. are shown for daily fish release rates. Planktonic regeneration rates are individual measurements and therefore, 95% C.I. are not shown.....79

Figure 4.1.4. N:P released by fish (mol:mol) in relation to dry mass (g), $n = 46$, $R^2 = 0.06$, $p = 0.10$, range 4.3:1 to 54.1:1 (mean = 18.1:1). Outlying data points for golden shiners are indicated.....80

Figure 4.1.5. Carbon, nitrogen and phosphorus content as a percentage of fish dry mass (g), $n = 47$. Each point represents a single fish. Note the log scale of the x-axis. Ranges of elemental composition were C 31.9% to 43.9% (mean = 39.3%), N 9.6% to 12.2% (mean = 10.9%) and P 2.1% to 5.3% (mean = 4.0%).....82

Figure 4.1.6. Mean mass (kg) of C, N and P per hectare bound in fish and plankton in Mouse and Ranger lakes from 1993 to 1995 (95% C.I. are shown). Carbon content of plankton was not measured.....84

Figure 5.1.1. The experimental protocol used in lake filtrate experiments. Epilimnetic lake water (20 l) was collected 1–2 m below the lake surface. Lake filtrate (<0.2 µm, 100 ml) was subjected to three experimental treatments (shade, PAR, PAR+UV). Incubations were conducted under ambient sunlight (2 h). The turnover time of the phosphate pool was measured after the samples had received one of the three experimental treatments.....107

Figure 5.1.2. The spectral absorbance of lake filtrate (<0.2 µm) that was exposed (incubated outdoors for 2 h) or unexposed (remained indoors) to direct sunlight. Spectral absorbance was measured at 1 nm wave lengths on a Cary 100 UV/VIS Scanning Spectrophotometer. Differences in the spectral absorbance were significant for all trials at all wave lengths (UVB, UVA, and PAR) ($p < 0.001$, t -test) for all lakes.....111

Figure 5.1.3. Lake filtrate (<0.2 µm) was subjected to three experimental treatments; shade, PAR, and PAR+UV. The turnover time of the phosphate pool (min ± 1 S.E) was measured after treatment. Treatment effects were analyzed with one-way ANOVA. When treatment effects were observed ($p < 0.05$) pairwise comparisons with Bonferroni corrections were performed. The turnover time of the phosphate pool in the PAR+UV treatment was significantly less than the shade and PAR treatments, but only for Muskoka and only on one date (July 16th).....113

Figure 5.2.1. Turnover time of the dissolved phosphate pool (min ± 1 S.D) after lake filtrate (<0.2 µm) was exposed to the experimental treatments: shade, PAR, or PAR+UVR. The turnover time of the phosphate pool was significantly greater for Upper Blackstrap L. Treatment effects were analyzed with one-way ANOVA. When treatment effects were observed ($p < 0.05$) Dunnet's pairwise comparisons (applying Bonferroni correction factors) with the control (shade treatment) were performed. Lakes increase in total P from left to right.....122

Figure 5.3.1. The experimental protocol. Surface lake water (20 l) was collected 1–3 m below the lake surface. Lake water (200–500 ml) was subjected to three experimental treatments (control, PAR, PAR+UVR). Incubations were conducted under sunlight (4–6 h). Triplicate incubation vessels ($n = 3$) were used for each set of controls and treatments.....131

Figure 5.3.2. Turnover time of the dissolved phosphate pool (min ± 1 S.D., $n = 3$) after lake water was exposed to experimental treatment (control, PAR, or PAR+UVR). Turnover times of the phosphate pool were greater in the PAR+UVR treatments compared to the control treatment. Note the uptake of ³³PO₄ was undetectable in PAR+UVR treatment of Lac la Peche. An effect of PAR on the turnover time of the dissolved phosphate pool was undetectable except for one lake (Lac la Peche) where turnover times were greater than in the control treatment. Differences between treatments

were determined with one-way ANOVA. Dunnet pairwise comparisons with a control were performed when significant differences ($p < 0.05$) between treatments were observed. * denotes values that are significantly different from the controls. Lakes increase in total P concentration from left to right.....140

Figure 5.3.3. The effect of treatment on the regeneration of dissolved P (A), the turnover rate of particulate P (regeneration rate \div particulate P concentration) (B), and the steady state phosphate concentration [$\text{ssPO}_4 = \text{regeneration rate} \div k$ (uptake constant)] (C) (± 1 S.D., $n = 3$) for lake water that had been exposed to control, PAR, or PAR+UVR treatments. * denotes values that are significantly different from the controls. Lakes increase in total phosphorus concentration from left to right.....141

Figure 5.3.4. An effect of UVR on the regeneration of dissolved P by plankton may be undetectable 4–12 h after incubation if plankton are capable of repairing rapidly (i.e., regeneration rates may need to be measured immediately after or during treatment to detect an effect of UVR). Therefore, we performed an additional set of experiments with plankton assemblages that were pre-labeled (~ 12 h incubation with $^{33}\text{PO}_4^{3-}$) prior to treatment. Shown are the effect of treatment on the regeneration of dissolved P (A), and the turnover of particulate P (regeneration rate \div particulate P concentration) (B) (± 1 S.D., $n = 3$) in lake water that had been exposed to experimental treatments (control, PAR, or PAR+UVR). Note regeneration rates for Delaronde and Cowan Lakes were measured under constant artificial UVR exposure (SunTest Solar Simulator, 250 Wm^{-2}). * denotes values that are significantly different from the controls.....143

Figure 5.3.5. Alkaline phosphatase activity in the dissolved fraction ($<0.2 \mu\text{m}$) (A) and particulate fraction ($>0.2 \mu\text{m}$) (B) (± 1 S.D., $n = 3$) in lake water that was exposed to one of three experimental treatments; control, PAR, or PAR+UVR. * denotes values that are significantly different from the controls. Lakes increase in total phosphorus concentration from left to right.....145

List of Tables

Table 2.1. Fish species, form of nitrogen (N) and phosphorus (P) measured, and the sample size (<i>n</i>) of fish used to model nutrient release. Measured forms of nutrients included ammonia N (NH ₃ -N), ammonium N (NH ₄ -N), total ammonia N (TAN), total dissolved P (TDP), soluble reactive P (SRP), total reactive P (TRP), and total P (TP). Different fish species were not identified in two studies (Andre et al. 2003; Meyer & Schultz 1985); for these studies the sample size of each species (<i>n</i>) was unknown. * indicates that a study presented release rates as a mean for a species of a specified fish mass. In studies presenting mean rates, <i>n</i> represents the number of mean rates available, whereas, in studies presenting rates of individual fish, <i>n</i> represents the number of individuals.....	14
Table 2.2. Empirical models for predicting the release of nutrients (N and P) by detritivorous and non-detritivorous fish as a function of fish wet mass (log or log(<i>x</i> +1)) and mean water temperature (°C). Multiple regression models were developed from direct measurements of the rate of nutrient release reported in the literature for 56 species of fish. Model selection was conducted with AIC.....	25
Table 2.3. Comparison of regression coefficients for nutrient release models reported across studies. Models for this study and for Paulson (1980) were derived from direct measurements of fish nutrient release. The multispecies model presented by Schindler and Eby (1997) was derived from bioenergetic modeling of fish release (na, data not available).....	31
Table 3.1. Empirical models for predicting the release of nutrients (N and P) by zooplankton, mussels, benthic macroinvertebrates and fish as a function of the logarithm of organism dry mass (mg) and mean water temperature (°C). Multiple regression models were developed from direct measurements of the rate of nutrient release reported in the literature. The number of different species in each model ranged from 11–74. Model selection was conducted with AIC. The partial correlations (<i>r</i>) are shown. Note that the nutrient release models for fish are derived from Sereda et al. (2008a) but are presented here (for comparison) as a function of organism dry mass.....	44
Table 3.2. Linear regression coefficients for rates of N and P excretion by metazoan assemblages obtained from published studies. Coefficients correspond to regressions presented in Fig 3.3.....	55
Table 4.1.1. Physical and chemical properties of Mouse and Ranger Lakes (from McQueen et al. 2001; Dillon et al. 2001). TP and TKN (Total Kjeldahl Nitrogen) are mean epilimnetic concentrations (1993-95).....	70
Table 4.1.2. Comparison with other studies of fish release rates of N, P and N:P release ratios (by moles). Nutrients released were NH ₄ -N (N) and TP unless otherwise stated. All rates, except one (Tarvainen et al. 2002) were determined by direct measurements of release.....	87

Table 4.1.3. Comparison of predicted TP and N (N in NH_4^+) release rates with release rates from other studies. Release rates presented as a range represent observed rates for all fish in the study. Predicted rates were calculated with our empirical fish release relationships (Fig. 1), and the fish wet mass reported in each study. TP, SRP, $\text{NH}_4\text{-N}$ and total ammonia nitrogen (TAN) were the release products measured from each study. Predicted release rates overlap with rates reported from other studies (* mean).....	91
Table 5.1.1. The physical and chemical properties for Muskoka, Brandy and Plastic Lakes (Welsh et al. 1996; Vander Zanden & Rasmussen 1999). Total iron (Fe), and nitrate concentrations represent ten year means (1988–2007) obtained from the Ontario Ministry of Environment’s Dorset Environmental Science Center. Total phosphorus (TP), total dissolved phosphorus (TDP) and dissolved organic carbon (DOC) concentrations are expressed as means plus standard errors (S.E.).....	104
Table 5.1.2. PAR and UVR were measured with a Biospherical BIC compact 4-channel radiometer (Biospherical Instruments, San Diego CA) at three wave lengths [305 nm, 320 nm, 340 nm, and for the entire photosynthetically active radiation spectrum (PAR)]. Vertical attenuation coefficients (k) were determined from the slope \ln (wavelength (nm) or PAR) as a function of depth. Attenuation coefficients are based on one measurement for Plastic L., and a mean of multiple measurements for L. Muskoka ($n = 3$) and Brandy L. ($n = 2$)......	105
Table 5.1.3. Total incident solar radiation for each experiment. Photosynthetically active radiation (PAR) and total ultraviolet radiation (UVA+UVB) were obtained from nearby meteorological field stations (Locke & de Grosbois 1986; Gennings et al. 2001).....	110
Table 5.1.4. Mean dissolved organic carbon (DOC) concentrations (\pm S.E) in the shade and the PAR+UV treatments. Significant changes in DOC concentration following treatment were not detected ($p \geq 0.21$, t -test). Specific UV absorbance (SUVA, Absorbance ₂₅₄ :DOC concentration) following treatment for each experimental lake are also shown. Larger SUVA ratios indicate a greater number of aromatic compounds in the lake water. A significant decline in SUVA for the PAR+UV treatment compared to the shade treatment was only observed for Plastic L. ($p = 0.035$, t -test).....	112
Table 5.2.1. Physical and chemical properties of the study lakes at the time of sampling.....	119
Table 5.2.2. Total incident solar radiation received by each experimental trial. Solar radiation measurements ($\text{KJ m}^{-2} \text{ h}^{-1}$) were taken with an Ocean Optics USB2000 radiometer. Values have been corrected for attenuation by acrylic filters.....	120
Table 5.2.3. The absorbance ratio 250:365 nm in lake filtrate exposed to one of two experimental treatments (shade, or PAR+UVR) for 6 h. Larger numbers indicate a decrease in the average molecular weight. Specific UV absorbance (SUVA,	

Absorbance₂₅₄:DOC concentration) following treatment for each experimental lake are also shown. Larger SUVA ratios indicate a greater number of aromatic compounds in the lake water. Numbers in bold indicate differences between shade and PAR+UVR treatments are significant at an alpha level of 0.05.....121

Table 5.3.1. Physical and chemical properties of the study lakes at the time of sampling. Note, Muskoka and Brandy Lakes are located in central Ontario, Canada. All other study lakes are located in Saskatchewan, Canada. nd = no data available.....129

Table 5.3.2. Total incident solar radiation received by each experimental trial. PAR and total UVR ($\text{KJ m}^{-2} \text{h}^{-1}$) was obtained from nearby meteorological field stations for the three Ontario Lakes (Muskoka, Plastic, and Brandy) during the 2007 experiments. Separate measurements of UVA and UVB were not available from the meteorological field stations for the 2007 data. All other solar radiation measurements ($\text{KJ m}^{-2} \text{h}^{-1}$) were taken with an Ocean Optics USB2000 radiometer. nd = no data available.....138

Chapter 1: Phosphorus in Limnetic Systems

1.1. Introduction

Phosphorus (P) is a key limiting nutrient regulating productivity in both freshwater and marine ecosystems. A full knowledge of the sources and pathways of the P cycle is essential for understanding aquatic ecosystem function and for managing eutrophication. Phosphorus is supplied to lakes from both external (tributaries, atmospheric, ground water, and anthropogenic) and internal sources (release from lake sediments, and regeneration by plankton and larger aquatic metazoans) (Fig.1.1). During the growing season internal supply routes become increasingly significant in supplying nutrients to primary producers. However, determining the significance of any one source (e.g., fish vs. macroinvertebrates vs. internal loading from the sediments, or detritivorous versus non-detritivorous species) has been a contentious topic (Hudson et al. 1999). Much of this debate reflects the fact that rates of nutrient input from different sources have not been compared in a comprehensive manner. This probably reflects the difficulty of simultaneously measuring rates of nutrient supply from multiple pathways.

Aquatic metazoans (i.e., fish and macroinvertebrates) excrete nutrients primarily in soluble form [ammonia (NH_3) and phosphate (PO_4^{3-})] that are readily available for uptake by primary producers (Kuenzler 1961; Peters & Lean 1973; Bayne & Scullard 1977; Kremer 1977; Biggs 1982; Kremer et al. 1986; Urabe 1993; Uthicke 2001; André, et al. 2003; Taylor 2010). However, the significance of nutrient release by fish for plankton assemblages is under debate (Mather et al. 1995; Hudson et al. 1999). Many authors have suggested that nutrient release by fish is significant (Brabrand et al. 1990; Kraft 1993; Persson 1997; Schaus et al. 1997; Schindler & Eby 1997), whereas others suggest it is not

(Kitchell et al. 1975; Nakashima and Leggett 1980; Hudson et al. 1999; Tarvainen et al. 2002; Bunnell et al. 2005; Griffiths 2006). The slow turnover times of P bound in fish biomass, relative to plankton suggests that fish may be important sinks rather than sources of P (Bartell & Kitchell 1978; Griffiths 2006).

Macroinvertebrates often represent a substantial fraction of metazoan biomass in aquatic ecosystems and may represent a significant internal regenerative pathway of nutrients (Nalepa et al. 1991; Kiibus & Kautsky 1996; Wilhelm et al. 1999). Rates of P release are expected to vary within and across taxa. While, intraspecific differences in rates of nutrients excreted by specific groups of macroinvertebrates have been studied (e.g. mussels) (Conroy et al. 2005), less is known about differences in excretion across a broader range of taxa (e.g., mussels vs. gammarids). Consequently, the significance of excretion across taxa in determining rates of P regeneration in aquatic ecosystems is unclear. Furthermore, the overall contribution of macroinvertebrates to the nutrient budget of lakes (relative to other sources, e.g., external loading) is poorly understood.

Another potentially important P pathway may be present from the photodecomposition of dissolved organic phosphorus (DOP) in surface waters (Fig. 1.1). The effect of ultraviolet radiation on the nitrogen and carbon cycle has been under investigation since the early 1990s. Yet, the significance of P released from the photodecomposition of organic carbon compounds that bind nutrients (DOP) is unknown and may represent a significant pathway because microbial resistant DOP compounds are found at concentrations in aquatic systems that are orders of magnitude greater than PO_4^{3-} . However, ultraviolet radiation (UVR) may also influence nutrient cycling biotically through changes in planktonic nutrient acquisition (Behrenfeld et al. 1995;

Hessen et al. 1995; Allen and Smith 2002; Aubriot et al. 2004; Lesser 2008). Under ambient conditions, the separation of abiotic and biotic effects on P kinetics may be confounded. For example, an increase in the turnover time of the PO_4^{3-} pool may occur as a result of an increase in PO_4^{3-} concentration (i.e., from the liberation of PO_4^{3-} from DOP), cellular damage that reduces the rate of P uptake by plankton, cell leakage from damaged organisms, or some combination of these factors. Consequently, experimental isolation of abiotic (changes in P availability) and biotic (changes in nutrient acquisition) effects would be informative.

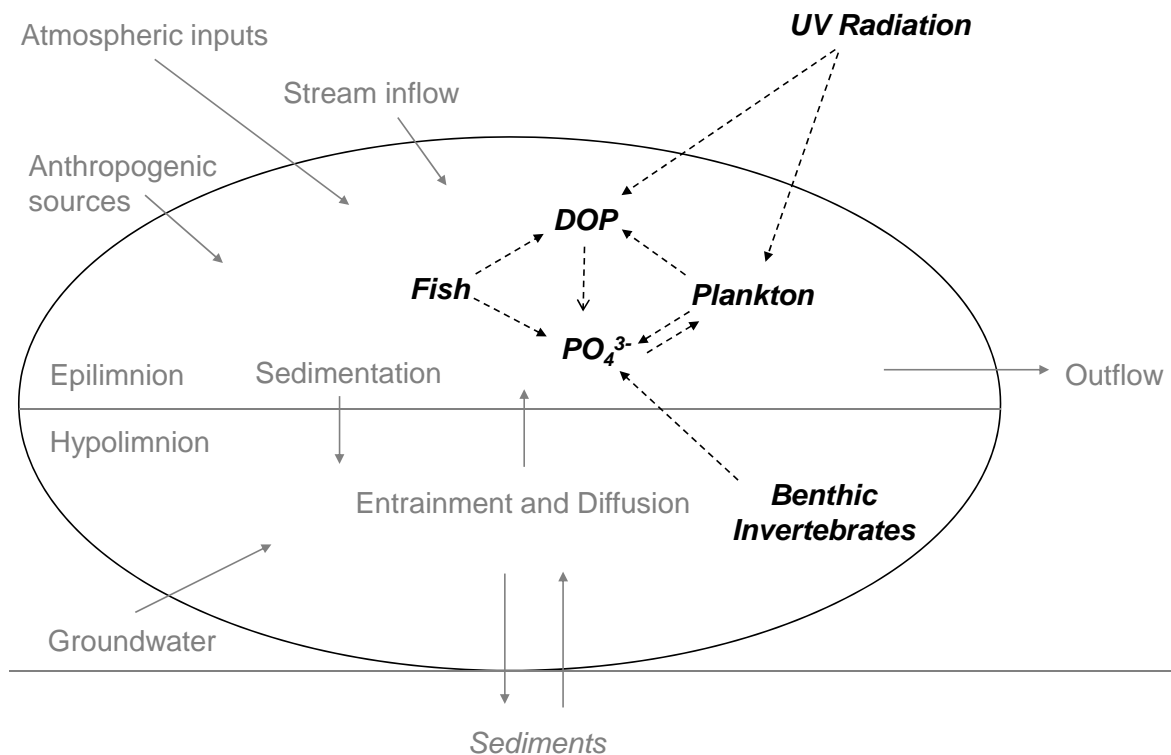


Figure 1.1. Diagram of the primary P pathways in lakes. Pathways in bold with dotted arrows signify pathways that have not been quantified or their significance to the overall nutrient budget are poorly understood.

1.2. Mass Balance Models

Mass balance models are commonly applied for measuring P fluxes in lake systems (Dillon et al. 1993; Soranno et al. 1997; Hakanson et al. 2003). Phosphorus supply routes such as atmospheric deposition, tributary inflow, anthropogenic sources, and internal loading from lake sediments are frequently measured and incorporated in P budgets. However, other potentially significant internal pathways exist (i.e. fish, macroinvertebrates, and photodecomposition processes), yet these are infrequently measured or remain uncharacterized (Fig 1.1).

A number of models have been developed for use in mass balancing (Canfield et al. 1982; Walker & Havens 2003; Nürnberg 1984). The following are examples of some of the commonly used models (Equations 1–4). However, variations of each model exist.

Equation 1: Water mass balance models (Walker & Havens 2003).

$$Q_o = Q_i + PA - EA + V_s - V_e$$

Q_o = lake outflow ($\text{m}^3 \text{d}^{-1}$)

Q_i = total inflow ($\text{m}^3 \text{d}^{-1}$)

P = precipitation (m d^{-1})

E = evaporation (m d^{-1})

A = surface area (km^2)

V_s = volume at start of day (m^3)

V_e = volume at end of day (m^3)

Equation 2: General P retention model:

$$(P_{\text{in}} - P_{\text{out}}) / P_{\text{in}} = \% \text{ retention}$$

Equation 3: Sedimentation model (Canfield et al. 1982).

$$\sigma = L (zTP) - p$$

σ = phosphorus sedimentation coefficient (d^{-1})

L = annual areal phosphorus loading ($\text{mg m}^{-2} \text{d}^{-1}$)

z = lake mean depth (m)

TP = concentration of total phosphorus in lake water (mg m^{-3})
p = hydraulic flushing rate (d^{-1})

Equation 4: Lake TP concentration model (Nürnberg 1984).

$$\text{TP} = L_{\text{ext}} / q_s (1 - R_{\text{pred}}) + L_{\text{int}} / q_s$$

TP = lake TP concentration (mg m^{-3})

L_{ext} = external load ($\text{mg m}^{-2} \text{d}^{-1}$)

L_{int} = internal load ($\text{mg m}^{-2} \text{d}^{-1}$)

q_s = areal water load (m d^{-1})

R_{pred} = predicted retention (mg d^{-1})

1.3. Frequently Measured Sources of Phosphorus

A number of P fluxes are commonly measured in the development of nutrient budgets.

The most common measurements are described below.

1.3.1. Groundwater

Accurate measurements of ground water inputs are often difficult to obtain (Nöges 2005). The contribution of groundwater to the overall nutrient and water budget is highly variable. Groundwater is frequently determined to be negligible to both the nutrient and water budget. Therefore, it is not often measured or rates of inflow are inferred from measurements obtained from other studies.

1.3.2. Atmospheric

Atmospheric inputs include both wet fall (precipitation) and dry fall (pollen, dust, insects, and leaves) (Graham et al. 2006). Typically dry fall contributes more P to the lake than wet fall (Jansson 1979; Morales-Baquero et al. 2006). Atmospheric deposition may be a significant source of P for oligotrophic systems (Jansson 1979; Morales-Baquero et al. 2006), enhancing algal growth and zooplankton abundance (Graham et al. 2006). However, atmospheric sources tend to become less important with increasing lake

productivity (Garber and Hartman 1985; Soranno et al. 1997), and increasing catchment to lake area ratios (Dillon et al. 1993).

1.3.3. Internal Loading

Lake sediments are important in the overall P budget of a lake, acting both as a sink and as a source (Bostrom et al. 1988). Phosphorus released from sediments has been found to be more biologically available than P derived from external sources (Nürnberg 1988). Therefore, internal loading may be a significant source of P supporting primary production during summer months, particularly for shallow lakes (Istvanovics et al. 2004). However, in deep lakes entrainment of P into the epilimnion will depend on water column stability (i.e. strength of the thermocline), and the concentration gradient between the hypolimnion and the epilimnion (Soranno et al. 1997). Therefore, the quantity of P actually entrained into the epilimnion may be low, despite accumulation of P in the hypolimnion (Soranno et al. 1997).

The significance of internal loading will vary with trophic status of the lake. The magnitude and duration of internal loading from lake sediments typically increases with lake productivity (Bostrom et al. 1988; Sondergaard 2001).

1.3.4. Tributaries

Major tributary inflows that contribute to both the water and nutrient budgets and are routinely included in mass balancing. Tributaries are commonly the largest external supplier of nutrients to lakes, particularly for systems with large watershed to lake area ratios. However, during summer months the quantity of nutrients exported to the lake from the watershed may decrease due to low precipitation and decreased water flows.

1.4. Infrequently Measured or Un-quantified Sources of Phosphorus

A number of potentially significant pathways in the P cycle of lakes are rarely measured or remained uncharacterized. These pathways are the focal point of this study, and are described below.

1.4.1. Fish

Fish release nutrients, mainly in soluble forms (PO_4^{3-} and NH_3) which are readily available to most plankton (Brabrand et al. 1990; Persson 1997b; Schaus et al. 1997; Attayde & Hansson 1999). Fish excretion may represent a significant source of nutrients during times of low external inputs (Brabrand et al. 1990; Kraft 1993; Persson 1997b; Schaus et al. 1997), enhancing primary production (Brabrand et al. 1990; Persson 1997a; Attayde & Hansson 1999; Attayde & Hansson 2001).

Fish also contain a substantial amount of P in their biomass which is unavailable to primary producers. For example, Kitchell et al. (1975) found up to 75% of total phosphorus (TP) in the pelagic zone of Lake Wingra (Wisconsin) was in fish biomass. In addition, the authors estimated that 30–35% of the annual input of P into Lake Wingra was sequestered into fish biomass. Parmenter and Lamarra (1991) estimated that 40% of the total fish P may remain immobilized in bone and scales which, upon death of the fish, may be incorporated into the sediment. Such studies suggest that fish may be considered sinks rather than sources of nutrients.

1.4.2. Macroinvertebrates

Macroinvertebrates may enhance nutrient fluxes indirectly through burrowing activities (Gardner et al. 1981; Fukuhara & Sakamoto 1988), and directly through excretion (Starkel 1985; Fukuhara & Yasuda 1989; Henry & Santos, 2008). Many

benthic macroinvertebrates feed on benthos during the day, and undergo vertical migrations at night releasing benthic derived nutrients into the epilimnia (Aneer 1980; Madeira et al. 1982; Wilhelm et al. 1999). Benthic-pelagic coupling by macroinvertebrates may represent a significant flux of nutrients particularly when invertebrate biomass is great (e.g. in fishless lakes) (Wilhelm et al. 1999). As such, the ability to estimate nutrient regeneration from benthic macroinvertebrates may be essential for advancing our understanding of nutrient fluxes in lakes.

1.4.3. Abiotic Effects of Ultraviolet Radiation

Dissolved organic phosphorus (DOP) is found at concentrations that are orders of magnitude greater than PO_4^{3-} in the epilimnia of lakes. The DOP pool may be a significant source of P when the dissolved inorganic P (DIP) pool becomes depleted (Thingstad et al. 1993; Monaghan 1999; Cavender-Bares 2001).

The bioavailability of dissolved organic matter (DOM) and associated nutrients (i.e., nitrogen (N) and P) may increase following ultraviolet radiation (UVR) exposure (Kieber et al. 1990; Mopper et al. 1991; Wetzel et al. 1995; Bushaw et al. 1996; Kieber 1999; Vahatalo et al. 2003). For example, the release of orthophosphate from dissolved organic matter following exposure to UVR has been reported in lake water (Francko & Heath 1979; Francko & Heath 1982; Cotner & Heath 1990; Zhou 1996). These studies used measurements of soluble reactive phosphorus (SRP) to determine increases in PO_4^{3-} concentration; SRP grossly overestimates PO_4^{3-} concentration (Hudson et al., 2000) and more advanced approaches (e.g., Hudson et al. 2000) are warranted to quantify this potentially important P pathway. For example, the concentration of the PO_4^{3-} pool is expected to increase through the photodecomposition of DOP to PO_4^{3-} . This rise in PO_4^{3-}

concentration should be detectable as an increase in the turnover time of the PO_4^{3-} pool (Lean & Nalewajko 1979; Lean 1984).

1.4.4. Biotic Effects of Ultraviolet Radiation

Phosphate is primarily supplied to pico- and nanoplankton through regenerative processes within planktonic assemblages (Hudson et al. 1999). Consequently, any process that alters rates of planktonic P regeneration may have a profound effect on the biogeochemical cycle of lakes (e.g., primary production). For example, planktonic uptake of N (Behrenfeld et al. 1995; Lesser 2008) and P (Hessen et al. 1995; Allen & Smith 2002; Aubriot et al. 2004) may be reduced following exposure to UVR. However, in a recent study by Allen and Smith (2002) an effect of UVR on the specific uptake of phosphate at ambient concentrations (turnover) was not detected despite reductions in phosphate saturated uptake rates. The authors suggested that both the uptake rate and ambient concentration of dissolved PO_4^{3-} may have been reduced by UVR, such that the specific uptake rate did not change significantly. The authors note that this may be possible if regeneration rates of dissolved P decreased more than the uptake rate. However, the effect of UVR exposure on the regeneration of dissolved P and on ambient PO_4^{3-} concentrations is currently unknown. A change in planktonic regeneration may also affect the turnover rate of the planktonic food-web (particulate P); however, this too has not been previously investigated.

1.5. Objectives

Advances in our understanding of the significance of aquatic metazoans in the nutrient dynamics of aquatic systems may be derived from empirical models which provide the ability to simultaneously estimate rates of nutrient fluxes. Such models would

complement other empirical models in the literature (e.g. Equations 1–4; Nürnberg 1988, Hudson et al. 2005). Rates of nutrient release by metazoans could then be compared with other nutrient fluxes (e.g. internal loading from the sediments and external loading from the watershed and atmosphere) and the significance of any single pathway could be determined. Therefore, my initial focus will be to develop a set of empirical models of nutrient release for aquatic metazoans (fish, zooplankton, mussels and other benthic macroinvertebrates). Models for both N and P release will be developed and discussed; however, my final summary (i.e., synthesis and discussion) will center on the contribution and significance of metazoans on P cycling.

Second, I will investigate and discuss the role of fish as sinks versus sources of nutrients in lakes. Fish biomass generally increases with lake productivity. Therefore, fish are expected to contribute more to the nutrient supply along the trophic gradient. However, increased biomass also results in increased quantities of P sequestered into tissue that is unavailable to primary producers. Therefore, it is expected once put into the context of other sources, fish will be found to be minor contributors to the overall nutrient budget.

I will also investigate the effect of UVR on pelagic P cycling. Initial experiments will examine the significance of the photodecomposition of DOP to PO_4^{3-} . This will clarify the role of photodecomposition of DOP relative to other internal pathways and provide researchers with a better understanding of the nutrient pathways supporting food webs. Finally, I will examine the direct effects of UVR on planktonic P kinetics (i.e., turnover time of the dissolved PO_4^{3-} pool, regeneration of dissolved P, turnover rate of particulate P and on steady state PO_4^{3-}).

Chapter 2: General Empirical Models for Predicting the Release of Nutrients by Fish¹

2.1. Introduction

Internal nutrient cycling (e.g., from plankton, fish and loading from sediments) can supply much of the requirements of algae and bacteria during the growing season (Kilham & Soltau-Kilham 1990; Hudson et al. 1999; Vanni et al. 2006). The contribution each pathway makes to the internal nutrient supply in lakes is expected to change along a trophic gradient. For example, Hudson et al. (1999) demonstrated that the regeneration of phosphorus (P) by planktonic food webs was a function of plankton biomass, and as plankton biomass increased along a trophic gradient so did the regeneration of nutrients by plankton (Hudson et al. 1999; Hudson & Taylor 2005). Internal loading of nutrients from lake sediments also increases with lake productivity (Bostrom et al. 1988; Sondergaard 2001). Griffiths (2006) noted that the release of nutrients by fish was a function of their biomass which also increased with lake productivity. However, it is not clear how the rates of nutrient cycling by each pathway change relative to one another along a trophic gradient. A comparison of these pathways may reveal when each pathway may be a significant contributor of nutrients. Empirical models have been developed to predict regeneration of P by the plankton (Hudson et al. 1999) and internal sediment loading (Nürnberg 1984) across lakes. Therefore, empirical models that provide an estimate of nutrient release by fish assemblages would allow for rapid comparisons with other internal cycling processes. In addition, such a model would help integrate nutrient regeneration processes with estimates of external nutrient supply; this in turn, would

¹ Contents of this chapter have been published in *Freshwater Biology*. 2008. **53**: 2133-2144.

provide limnologists and lake managers with a more comprehensive understanding of nutrient supply pathways to bacteria and algae across a diversity of lakes.

Direct measurement and bioenergetic modeling have been used to estimate the rates of nutrient release by fish assemblages (Kraft 1992; Gido 2002; Zimmer et al. 2006). While each method provides precise measurements of nutrient release, neither lends itself to the rapid estimation of nutrient release across systems. For example, knowledge of consumption and growth, plus the nutrient and energy content of both predator and prey species are required for bioenergetic modeling (Kraft 1992). Moreover, direct measurement techniques require fish from a broad range in mass to be captured and incubated in containers for substantial periods (generally ≥ 1 h) (Schaus et al. 1997; André et al. 2003; Sereda et al. 2008a). In addition, release rates must be measured several times over the season or year to capture the variation in rates due to changes in water temperature and feeding.

Rates of nitrogen (N) and P release by individual fish have been reported to be strongly correlated with fish mass (André et al. 2003; Higgins et al. 2006), water temperature (Forsberg & Summerfelt 1992; Schaus et al. 1997) and diet (Beamish & Thomas 1984; Schindler & Eby 1997; Torres & Vanni 2007). Empirical models that capture the variability in release rates attributable to these factors for a diversity of fish species may provide a relatively quick means to predict the release of nutrients by fish and, therefore, eliminate the need for more complex and time-consuming approaches.

An empirical relationship that permits the rapid prediction of the release of nutrients by fish assemblages was presented by Sereda et al. (2008a); however, this model was based on only five fish species, across a relatively narrow range in fish wet mass (1.3–

205.5 g), and over a small range in temperature (23–26 °C). Furthermore, these models did not include detritivorous species, which have been reported to release greater quantities of nutrients (Brabrand et al. 1990; Torres & Vanni 2007) than planktivorous fish. Furthermore, many fish undergo ontogenetic (Higgins et al. 2006), biomass-dependent (Schaus et al. 2002), and seasonal dietary shifts (Mehner et al. 1998), alternating between planktivorous and detritivorous feeding habits according to prey availability (Schaus et al. 2002). During periods of planktivory, the contribution of fish to the nutrient supply in lakes is expected to be less than that during periods of detritivory. Therefore, separate models of nutrient release for detritivores and non-detritivores may improve model precision, and provide researchers with a quick estimate of the effect of dietary shifts on the total quantity of nutrients released.

Our study had five objectives. First, to review the literature and develop models which include more fish species, across a broader range in fish mass and over a broader range in water temperature. Second, to develop empirical models that provide precise estimates of nutrient release (N and P) by fish assemblages across diverse habitats (e.g., varying in trophic status). Third, to develop separate models for detritivores and non-detritivores in an attempt to improve model precision. Fourth, to test the empirical models with an independent data set, and finally, to estimate the change in total nutrients released when gizzard shad (*Dorosoma cepedianum* L.), a facultative detritivore, is 100% detritivorous or 100% non-detritivorous.

2.2. Methods

We obtained directly measured release rates for 56 temperate and tropical, marine and freshwater species from the literature (Table 2.1). Rates obtained from each study were

either for individual fish or were species means. Mean release rates will be influenced by the range of fish mass used to obtain the mean rate. Fish of similar size were pooled together in studies presenting rates as species means (e.g., Vanni et al. 2002), thus mean rates should be characteristic of a species of a specific mass. We extracted release rates using data mining software (GetData Graph Digitizer v. 2.22, <http://get-data-graph-digitizer.com>) when data were only presented in plotted figures. Release rates were obtained for both wild (Lamarra 1975; André et al. 2003; Zimmer et al. 2006) and cultured fish (Jatteau et al. 1997). Different fish species were not always distinguished in multi-species studies in figures. (Meyer & Schultz 1985; André et al. 2003). Fish in such studies were grouped under the general headings of Haemulidae or Cichlidae, respectively (Table 2.1).

Table 2.1. Fish species, form of nitrogen (N) and phosphorus (P) measured, and the sample size (*n*) of fish used to model nutrient release. Measured forms of nutrients included ammonia N (NH₃-N), ammonium N (NH₄-N), total ammonia N (TAN), total dissolved P (TDP), soluble reactive P (SRP), total reactive P (TRP), and total P (TP). Different fish species were not identified in two studies (André et al. 2003; Meyer & Schultz 1985); for these studies the sample size of each species (*n*) was unknown. * indicates that a study presented release rates as a mean for a species of a specified fish mass. In studies presenting mean rates, *n* represents the number of mean rates available, whereas, in studies presenting rates of individual fish, *n* represents the number of individuals.

Study	Species	Form of N	<i>n</i>	Form of P	<i>n</i>
		measured		measured	
Non-detritivores					
Sereda et al. 2008a	<i>Notemigonus crysoleucas</i> Mitchill	NH ₄ -N	7	TP	9

	<i>Lepomis gibbosus</i> Linnaeus		10		10
	<i>Perca flavescens</i> Mitchill		10		10
	<i>Micropterus salmoides</i> Lacepède		10		10
	<i>Catostomus commersonii</i> Lacepède		9		9
Lamarra 1975	<i>Cyprinus carpio</i> Linnaeus			SRP	31
*Vanni et al. 2002	<i>Ancistrus triradiatus</i> Eigenmann	NH ₃ -N	2	TDP	2
	<i>Chaetostoma milesi</i> Fowler		3		3
	<i>Farlowella vittata</i> Myers		2		2
	<i>Hypostomus</i> sp.		2		2
	<i>Lasiancistrus</i> sp.		2		2
	<i>Spatuloricaria</i> <i>gymnogaster</i> Eigenmann & Vance		2		2
	<i>Leporinus striatus</i> Kner		2		2
	<i>Bunocephalus amaurus</i> Eigenmann		1		1
	<i>Pseudocetopsis</i> sp.		1		1
	<i>Astyanax integer</i> Myers		2		2
	<i>Astyanax metae</i> Eigenmann		1		1
	<i>Bryconamericus</i>		2		2

	<i>deuterodonoides</i> Eigenmann				
	<i>Cheirodon pulcher</i> Gill		2		2
	<i>Cheirodontops geayi</i> Schultz		1		1
	<i>Creagrutus beni</i> Eigenmann		2		2
	<i>Gephyrochyrax Valencia</i> Eigenmann		1		1
	<i>Roeboides dayi</i> Steindacher		1		1
	<i>Characidium boaevistae</i> Steindacher		1		1
	<i>Aquidens pulcher</i> Gill		1		1
	<i>Crenicichla</i> sp.		1		1
	<i>Cyphocharax spiluris</i> Günther		1		1
	<i>Parodon apolinari</i> Myers		3		3
	<i>Microglanis iheringi</i> Gomes		1		1
	<i>Pimelodella</i> sp.		2		1
	<i>Ochmanthus alternus</i> Myers		1		1
	<i>Trichomycterus</i> sp.		1		1
Gido 2002	<i>Ictiobus bubalus</i> Rafinesque	NH ₃ -N	15	TRP	16
*Andre et al. 2003	Cichlidae	NH ₄ -N	22	SRP	34
	<i>Pseudotropheus tropheops</i> Regan				

	<i>Petrotilapia</i> sp.				
	<i>Labeotropheus fuelleborni</i> Ahl				
	<i>Cynotilapia afra</i> Günther				
	<i>Pseudotropheus zebra</i> Boulenger				
*Brabrand et al. 1990	<i>Rutilus rutilus</i> Linnaeus			SRP	9
	<i>Perca fluviatilis</i> Linnaeus				1
*Tarvainen et al. 2005	<i>Gymnocephalus cernus</i> Linnaeus	NH ₄ -N	9	SRP	9
*Meyer & Schultz 1985	Haemulidae	NH ₄ -N	29		
	<i>Haemulon Flavolineatum</i> Desmarest				
	<i>Haemulon plumieri</i> Lacepède				
*Yager & Summerfelt 1993	<i>Stizostedion vitreum</i> Mitchell	NH ₄ -N	82		
*Jatteau 1997	<i>Acipenser baeri</i> Brandt	TAN	14		
*Bray et al. 1988	<i>Chromis punctipinnis</i> Cooper	NH ₄ -N	2		
	<i>Paralabrax clathratus</i> Girard		1		
	<i>Semicossyphus pulcher</i> Ayres		1		
	<i>Alloclinus holderi</i> Lauderbach		1		

	<i>Coryphopterus nicholsi</i> Bean		1		
	<i>Lythrypnus dalli</i> Gillbert		1		
	Detritivores				
Higgins et al. 2006	<i>Dorosoma cepedianum</i> Lesueur	NH ₄ -N	202	SRP	210
Gido 2002	<i>Dorosoma cepedianum</i>	NH ₃ -N	15	TRP	15
	<i>Carpiodes carpio</i> Rafinesque	NH ₃ -N	10	TRP	10
Schaus et al. 1997	<i>Dorosoma cepedianum</i>	NH ₃ -N	63	SRP	62
*Brabrand et al. 1990	<i>Rutilus rutilus</i>			SRP	3
	<i>Abramis brama</i> Linnaeus				1
*Zimmer et al. 2006	<i>Pimephales promelas</i> Rafinesque	NH ₃ -N	81	TDP	84

Nutrient release rates that were only presented as mass-specific release rates ($\mu\text{g g}^{-1} \text{h}^{-1}$), or as molar release rates ($\mu\text{mol h}^{-1}$), were converted to μg nutrients released $\text{h}^{-1} \text{fish}^{-1}$. We only selected release rates of ammonium nitrogen (NH₄-N) and soluble reactive phosphorus (SRP) from each study when multiple forms of a nutrient were available. We selected the measurements of the dissolved form of N and P (e.g., total dissolved N (TDN), or total dissolved P (TDP)) when measurements of NH₄-N and SRP were not available. In addition, total P (TP) was the only measurement of P available for one study (Sereda et al. 2008a).

Incorporating different forms of a nutrient (e.g., SRP vs. TDP) into the model could introduce variability. However, measurements of NH_4 and SRP closely approximated measurements of TDN and TDP, respectively, accounting for nearly all dissolved N and P released (Jobling 1981; Beamish & Thomas 1984; Brabrand et al. 1990; André et al. 2003). Measurements of TP may have included some egested faecal matter, although, in this study P samples were extracted with a syringe through an external outlet above the bottom of the incubation container. Only minor quantities of particulate P would have been extracted because most faecal matter would have settled to the bottom. Therefore, each form of nutrient in this study should provide approximate measurements of the release of total dissolved nutrients. Measurements of basal excretion rate (a measure of N or P excretion when a fish is deprived of dietary N or P) were not included in our models, as these measurements require fish to undergo a period of starvation and would not be representative of rates measured under field conditions.

We separated fish species into two broad classes (detritivores and non-detritivores) based on descriptions of diet provided in each study (Table 2.1). The percentage of detritus in the diet of detritivores ranged between 50% and 90% (Gido 2002; Zimmer et al. 2006). Further divisions of the data into planktivores and piscivores may be justified in subsequent studies, but due to limitations of the current data this was not attempted here.

Two studies provided incomplete temperature data (Vanni et al. 2002; André et al. 2003). Therefore, a mean water temperature was obtained from associated studies (McKaye 1983; Flecker 1996). A range in mean water temperature of 15–29°C (detritivores) and 17–29°C (non-detritivores) was obtained from all studies.

We log-transformed release rates and fish wet mass (\log or $\log(x + 1)$) to normalize variance (Zar 1999). We then modeled nutrient release rates using multiple linear regression with individual fish mass and temperature as model predictors. Tolerance (a measure of collinearity between independent variables) ranged from 0.839–0.995; however, interaction terms exhibited significant multicollinearity with both fish mass and water temperature (tolerances ranged from 0.012–0.020) and, therefore, we did not consider second-order terms. We used Akaike's Information Criterion (AIC) to select the most parsimonious model among candidate models (balancing simplicity and predictive power) containing the null (intercept only), single-predictor (either fish mass or temperature), and two-predictor equations (Burnham & Anderson 2002). AIC is defined as: $-2(\log\text{-likelihood}) + 2k$, where k is the number of estimable parameters of the model in question. We ranked models according to the distance in AIC units of each model relative to the best model ($\Delta\text{AIC} = \text{AIC}_i - \min \text{AIC}$, where AIC_i is the value for model i , and the $\min \text{AIC}$ is the value of the best model). Here, $\Delta\text{AIC} < 2$ gives support for a candidate model; whereas, ΔAIC values between 3 and 7 provide considerably less support, and $\Delta\text{AIC} > 10$ indicates that the model is improbable (Burnham & Anderson 2002). Regression surfaces were developed independently of the regression models using locally weighted regression (LOESS), where the dependent variable (nutrient release rate) is smoothed as a function of the independent variables (fish mass (g) and water temperature ($^{\circ}\text{C}$)) in a moving fashion (Cleveland & Delvin 1988) (Fig. 2.1).

We then compared the slopes of fish mass (g) versus temperature normalized nutrient release rate with the theoretical slope of 0.75, as predicted by metabolic theory (Brown et al. 2004; Brown et al. 2007). Nutrient release rates were temperature corrected (metabolic

rate $\times e^{E/kT}$; where E is the average activation of metabolic reactions (0.65eV), k is Boltzman's constant (8.63×10^{-5} eV/K), and T is absolute temperature in Kelvin (Gillooly et al. 2001; Brown et al. 2007)). Slopes of fish mass (g) versus temperature corrected nutrient release rate were then estimated with standardized major axis regression (SMA) (<http://www.bio.sdsu.edu/pub/andy/RMA.html>) (Warton et al. 2006). SMA has been suggested as a superior alternative to ordinary least squares regression for bivariate line-fitting of allometric relationships (Warton et al. 2006).

The release of P by fish assemblages ($\text{g ha}^{-1} \text{d}^{-1}$) has been reported to be a positive linear function of fish biomass (kg ha^{-1}) (Griffiths 2006). A test of our model's utility can be obtained by applying it to an independent data set. In such a test, a linear relationship with a slope and intercept not significantly different from the relationship in Griffiths (2006) should be obtained. Therefore, we applied our models to a set of lakes where fish biomass and abundance had been measured (Bachmann et al. 1996). Selection of a model to apply to a particular fish species was based on the feeding habit to which that species (i.e., detritivore or non-detritivore) had previously been allocated (Schulz et al. 1999). To obtain a predicted daily release rate ($\mu\text{g nutrient h}^{-1} \text{individual}^{-1}$) we inserted into our models the mean wet mass (g) of each fish species. We then multiplied the number of individuals of a particular species present in a lake by the mean daily release rate of an individual to provide a total daily release by that species. We summed release rates for all species present and standardized to grams of nutrient released per hectare per day ($\text{g nutrient ha}^{-1} \text{d}^{-1}$). Lake temperature was unknown for most of the data in Griffiths (2006) relationship. Two of the studies (Persson 1997; Horppila 1998) reported mean water temperatures of approximately 20°C. Therefore, a temperature of 20°C was used to

predict release rates with our models. The relationship between fish biomass (kg ha^{-1}) and nutrient release rate ($\text{g nutrient ha}^{-1} \text{d}^{-1}$) (linear regression) was compared to that found in Griffiths (2006). Three studies in the Griffith's (2006) relationship were not independent from our model (Brabrand et al. 1990; Schaus et al. 1997; Gido 2002) and were removed prior to comparison. An independent data set for N release by fish assemblages was not available for a similar comparison.

Many fish species undergo dietary shifts (Bergman 1990; Mehner et al. 1998; Schaus et al. 2002) which may influence nutrient cycling in lakes (Mehner et al. 1998). Gizzard shad are facultative detritivores that shift between planktivory and detritivory (Schaus et al. 2002). Therefore, the gizzard shad is an ideal species to illustrate the effect of each diet-type on the quantity of nutrient that would be released under either scenario. We modeled the change in nutrient release by fish assemblages, when gizzard shad in the assemblage were 100% detritivorous or 100% non-detritivorous. Fish assemblage data were obtained from Bachmann et al. (1996), and the analysis was restricted to the 21 lakes where gizzard shad were present. Statistical analysis was performed with Statistica v. 6.1 (StatSoft, Inc., Tulsa, Oklahoma) and all significance levels were set at an alpha of 0.05.

2.3. Results

The mass of detritivorous fish ranged from 0.11–1375 g and of non-detritivorous fish from 0.38–3195 g. The logarithm of fish mass explained most of the variation (78–96%) in the release rate of each nutrient in both models (Fig. 2.1; Table 2.2). Temperature was a significant, but minor, variable in explaining the variation in nutrient release rates (Table 2.2). Temperature only increased the coefficient of determination for each model

by ~1–2%. Q_{10} values for N and P release rates were calculated by applying our models to a constant fish mass and varying water temperature. Q_{10} values ranged from 1.31 to 1.91.

We present only full, additive models (i.e., intercept plus both fish mass and temperature as predictors) based on model selection using AIC (Table 2.2). The full model for non-detritivore P release was only 0.67 AIC units greater than the next-best model (fish mass only); suggesting that water temperature marginally improved the predictive power of this model. In all other cases, full models (fish mass and water temperature) were superior to the next-best model by at least 7 AIC units (7–40). Slopes and intercepts were significantly different between detritivore and non-detritivore N-release models (t -test, $p < 0.001$); however, only intercepts were significantly different between the two P-release models (t -test, $p < 0.001$). Detritivorous fish exhibited an increased release rate relative to non-detritivorous fish for both nutrients (Fig. 2.1).

The slopes of fish mass (g) versus temperature corrected nutrient release rate estimated by SMA (Warton et al. 2006) were; 0.92 (± 0.032 , 95% C.I) and 0.79 (± 0.059 , 95% C.I) for non-detritivore N and P, and 0.76 (± 0.052 , 95% C.I) and 0.78 (± 0.033 , 95% C.I) for detritivore N and P, respectively.

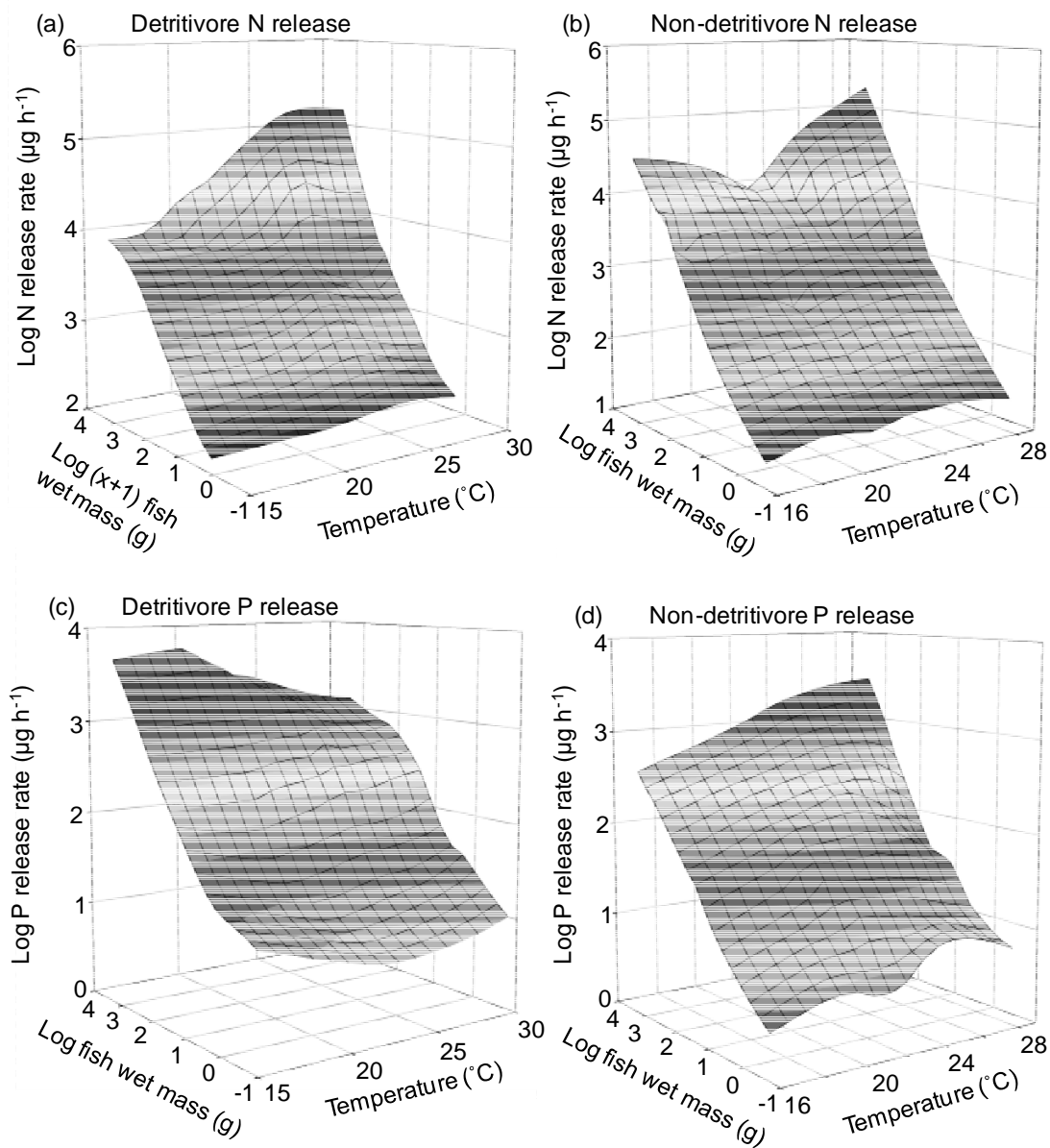


Figure 2.1. The release of nutrients ($\mu\text{g h}^{-1}$ of N or P) by detritivores and non-detritivores as a function of fish wet mass (log (mass (g)) or log (mass+1 (g)) and water temperature ($^{\circ}\text{C}$). Note that fish mass is a better predictor of nutrient release than water temperature. Figures were produced with smoothed data, LOESS function, SigmaPlot v. 9. (Systat Software, Inc., Chicago, IL.).

Table 2.2. Empirical models for predicting the release of nutrients (N and P) by detritivorous and non-detritivorous fish as a function of fish wet mass (log or log(x+1)) and mean water temperature (°C). Multiple regression models were developed from direct measurements of the rate of nutrient release reported in the literature for 56 species of fish. Model selection was conducted with AIC.

	Coefficient	S.E	t-statistic	<i>p</i>	Partial Correlation (<i>R</i>)
Detritivore N release model: (<i>n</i> = 371, $R^2 = 0.79$, $p < 0.001$)					
Intercept	1.861	0.076	24.475	< 0.001	
Log (x+1) fish wet mass (g)	0.728	0.021	34.227	< 0.001	0.872
Mean water temperature (°C)	0.012	0.003	3.642	< 0.001	0.187
Non-detritivore N release model: (<i>n</i> = 260, $R^2 = 0.93$, $p < 0.001$)					
Intercept	0.806	0.117	6.884	< 0.001	
Log fish wet mass (g)	0.876	0.016	56.451	< 0.001	0.962
Mean water temperature (°C)	0.028	0.004	5.708	< 0.001	0.386
Detritivores P release model: (<i>n</i> = 384, $R^2 = 0.88$, $p < 0.001$)					
Intercept	0.957	0.068	14.062	< 0.001	
Log fish wet mass (g)	0.769	0.015	50.836	< 0.001	0.934
Mean water temperature (°C)	0.012	0.003	3.871	< 0.001	0.195
Non-detritivore P release model: (<i>n</i> = 188, $R^2 = 0.82$, $p < 0.001$)					
Intercept	0.405	0.150	2.711	0.007	

Log fish wet mass (g)	0.733	0.026	28.576	< 0.001	0.903
Mean water temperature (°C)	0.013	0.006	2.193	0.03	0.159

To test our models, we applied them to a set of lakes where fish biomass and abundance had been measured. Rates of P release ($\text{g ha}^{-1} \text{d}^{-1}$) by fish assemblages were calculated as a function of fish biomass (kg ha^{-1}) (Fig. 2.2). Predicted release rates were then compared to an independent data set (Griffiths 2006). The slopes and intercepts (model I linear regression) of our predicted release rates and the observed rates in Griffiths (2006) were not significantly different (t -test, $p = 0.14$, and $p = 0.50$, respectively).

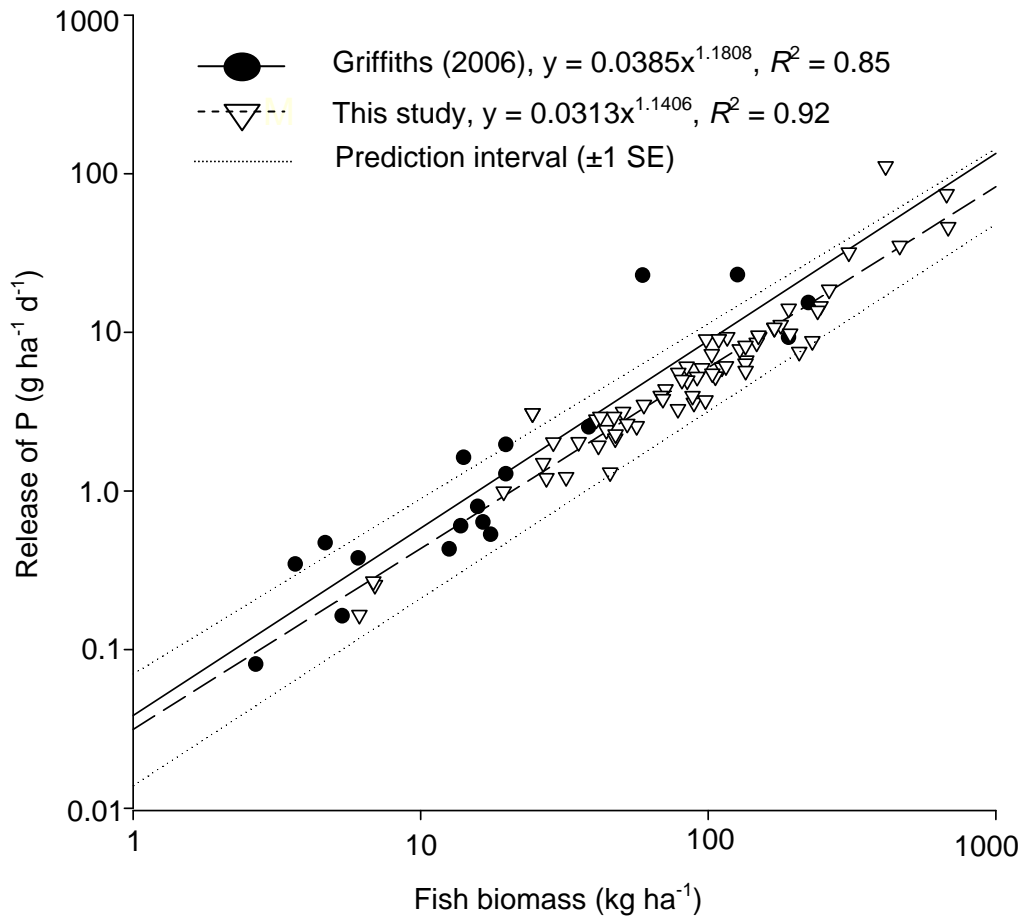


Figure 2.2. Predicted release rates of P ($\text{g ha}^{-1} \text{d}^{-1}$) ($n = 57$) in relation to total fish biomass (kg ha^{-1}), compared with rates for other lakes obtained from Griffiths (2006) ($n = 18$). Regressions (± 1 standard error of model regression coefficients) are shown for our predicted release rates. Error regressions should be conservative estimates as it is unlikely that the true values will vary in the same direction and magnitude. Slopes and intercepts are not significantly different between the two relationships (t-test, $p > 0.05$). Data were not available to make a similar comparison for nitrogen release.

Gizzard shad comprised an average of 23% of the total fish biomass (<1–75%) when present. Gizzard shad (when present) accounted for a large quantity of the total nutrients released averaging 39% (<1–96%) and 40% (<1–95%) of total N and P released, respectively, when modeled as detritivores. The total quantity of nutrients released (g ha^{-1}

d^{-1}) during periods of detritivory increased by an average of 56% (<1–331%) and 62% (<1–211%) (Fig. 2.3) for N and P, respectively in the whole fish assemblage.

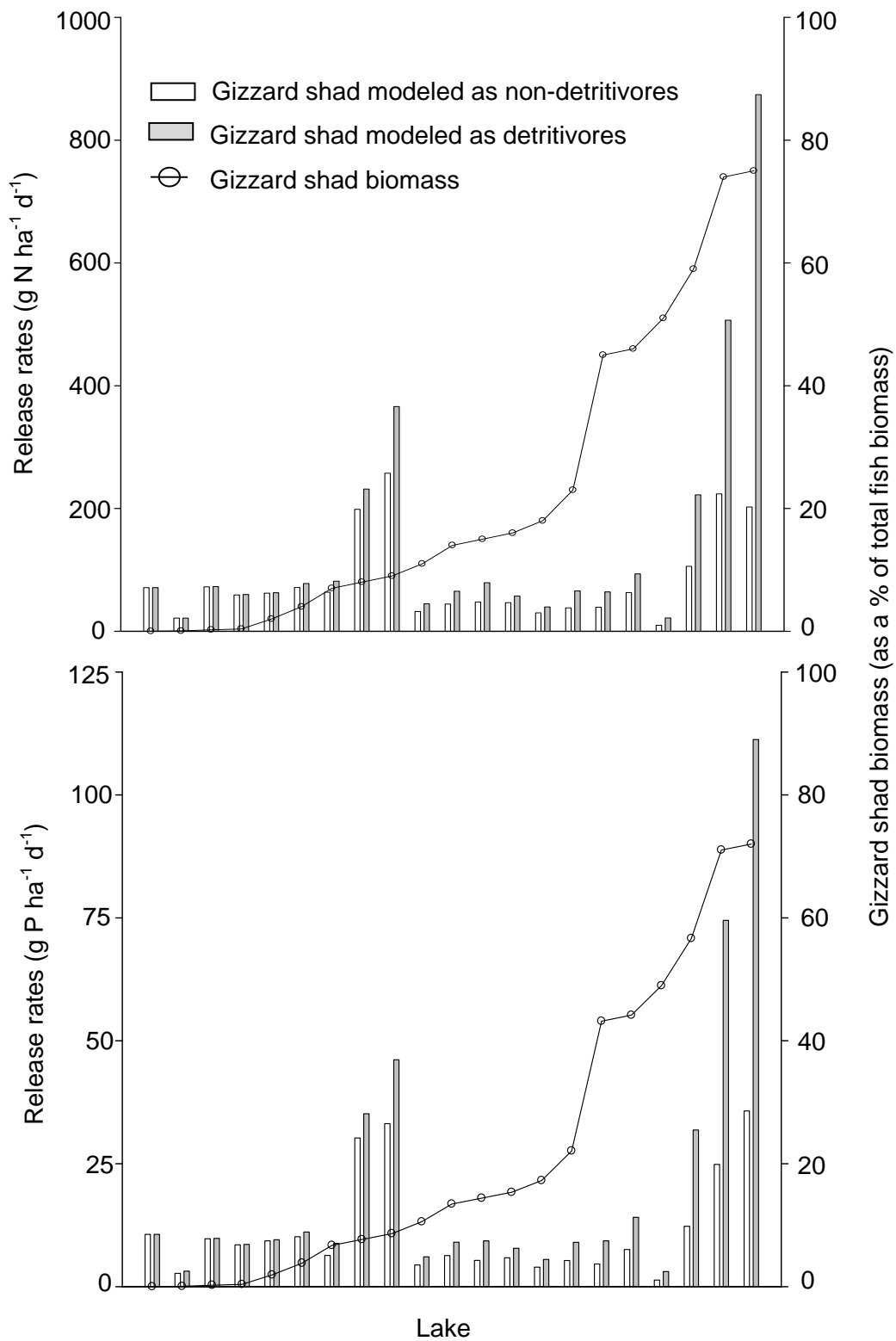


Figure 2.3. Comparison of N and P release rates when gizzard shad were modeled as 100% planktivores or 100 % detritivores. Fish assemblage data were obtained from Bachmann et al. (1996), and analysis was restricted to the 21 lakes where gizzard shad

were present. Gizzard shad accounted for an average of 23% (<1–75%) of total fish biomass in these lakes. Lakes are ordered such that gizzard shad biomass increases from left to right on the x-axis (as a % of total fish biomass). The total quantity of nutrients released increased by an average of 56% (<1–331%) and 62% (<1–211%) for N and P, respectively, when gizzard shad were solely detritivorous. Note that these rates would be representative of average rates if fish had these diets.

2.4. Discussion

We have developed the first multi-species empirical models of fish nutrient release (N and P) based on feeding habit (detritivores and non-detritivores). These models incorporate direct measurements of release rates for a total of 56 marine and freshwater species, and capture the variation in release rates that may be attributable to feeding histories, species composition, individual fish mass and water temperature.

Rates for individuals or species means were both used in our models depending on available data. Regression coefficients of fish wet mass in relation to P release rate were obtained from two studies, one using measurements of individual fish from temperate lakes (Sereda et al. 2008a) and the other from species means from a tropical river (Vanni et al. 2002). These values were almost identical at 0.793 and 0.782, respectively. Regression coefficients obtained from our multiple regression models for fish mass and water temperature were similar to coefficients derived from both multi-species bioenergetic (Schindler & Eby 1997) and individual species (Paulson 1980) models (Table 2.3). Furthermore, predicted coefficients of fish mass in relation to temperature corrected N and P release were close to the theoretical value of 0.75, as predicted by the metabolic theory of ecology (Brown et al. 2004). Thus, it appears that the use of both species means and individual measurements did not unduly influence our models.

Table 2.3. Comparison of regression coefficients for nutrient release models reported across studies. Models for this study and for Paulson (1980) were derived from direct measurements of fish nutrient release. The multispecies model presented by Schindler and Eby (1997) was derived from bioenergetic modeling of fish release (na, data not available).

Variable	Study	Species	Nitrogen model		Phosphorus model	
			Coefficients	± 95% C.I	Coefficients	± 95% C.I
Intercept	This study	Detritivores	1.861	0.150	0.957	0.134
		Non-detritivore	0.806	0.229	0.405	0.295
	Paulson 1980	Rainbow trout	1.123	na	na	na
		Brook trout	0.977	na	na	na
	Schindler & Eby 1997	Multispecies	-3.256	0.165	-4.776	0.134
Fish mass	This study	Detritivores	0.728	0.031	0.769	0.030
		Non-detritivore	0.876	0.031	0.733	0.051
	Paulson 1980	Rainbow trout	0.616	0.174		
		Brook trout	0.467	0.278		
	Schindler & Eby 1997	Multispecies	0.893	0.041	0.902	0.047
Temperature	This study	Detritivores	0.012	0.007	0.012	0.006
		Non-detritivore	0.028	0.008	0.013	0.012
	Paulson 1980	Rainbow trout	0.016	0.012	na	na
		Brook trout	0.035	0.028	na	na

Schindler & Eby 1997	Multispecies	0.014	0.006	0.008	0.006
----------------------------	--------------	-------	-------	-------	-------

Q_{10} values predicted from our models ranged from 1.31–1.91 and, although they were at the low end of rates in the literature (1.5–2.5) (Vanni 2002), they do overlap. We note, however, that the range of temperature in our study was only 14°C and may not have been sufficient to capture large shifts in metabolic rate. Temperature contributed more to the prediction of N release rates than the release of P (Table 2.2). Nitrogen release may be strongly affected by the rate of protein catabolism and deamination (Jobling 1981). Both metabolic processes are known to be largely influenced by temperature (Jobling 1981). Therefore, metabolic rate and hence temperature may have a greater effect on release rates of nitrogen than of P (Mather et al. 1995).

Verant et al. (2007) suggested that temperature may have a minor influence on the release rates by fish assemblages. Therefore, we assessed the effects of temperature on modeled release rates. Release rates of N and P increased on average by 35% and 15%, respectively, as a result of a 5°C increase in water temperature. While this change may be minor relative to changes in fish density and diet (Fig. 2.3), inclusion of water temperature in empirical models should improve the overall precision of nutrient release estimates.

Our models predicted P release rates ($\text{g ha}^{-1} \text{d}^{-1}$) in relation to total fish biomass (kg ha^{-1}) that were not significantly different from those reported in Griffiths (2006) (t -test, $p > 0.05$) (Fig. 2.2). Fish assemblages in the relationship produced by Griffiths (2006) were dominated by salmonids, centrarchids or cyprinids; whereas fish assemblages in the

present paper were dominated by centrarchids, clupeids and ictalurids (Bachmann et al. 1996). The lack of difference between relationships supports the suggestions of Griffiths (2006) and Verant et al. (2007) that species composition may contribute little to variation in release rates when a broad range of fish assemblage biomass is considered. However, it should be noted, across a smaller range in fish assemblage biomass a change in species composition (e.g., addition or loss of a detritivorous species) may have a large influence on fish nutrient release rates (McIntyre et al. 2007).

As observed here, Torres and Vanni (2007) also found that detritivorous fish made a greater contribution to the nutrient supply of lakes than non-detritivores. However, while past studies have emphasized the importance of detritivory to nutrient supply in lakes (Higgins et al. 2006; Vanni et al. 2006), they have not quantified the change in total nutrients released when detritivores switch to non-detritivory or *vice-versa*. For example, when gizzard shad were modeled as detritivorous, the total quantity of nutrients released increased on average by 56% (<1–331%) and 62% (<1–211%) (Fig. 2.3) for N and P, respectively. The greater average increase in P release, as gizzard shad shift from a planktivorous to a detritivorous feeding habit, would result in a declining N:P release ratio, which is consistent with the recent findings of Pilati and Vanni (2007).

When estimating release rates, we assumed all gizzard shad in our model made a complete shift from one feeding habit to the other. This probably resulted in an overestimate in release rates, but illustrates the importance of detritivory to the overall nutrient supply in lakes, particularly in lakes where gizzard shad are abundant. For example, gizzard shad accounted for 75% of total fish biomass in Hunter Lake and, if we assume that only 10% of the gizzard shad population switched from a planktivorous

feeding habit to one of detritivory, the release of nutrients by the fish assemblage would still increase by 33% and 21%, for N and P respectively, in Hunter Lake. The large influence that detritivory has on nutrient release rates indicates that detritivores and non-detritivores should be modeled separately.

Fish assemblage composition has been found to change along a productivity gradient (Bachmann et al. 1996; Olin et al. 2002). For example, as TP concentration increases, the abundance of cyprinid species (roach, *Rutilus rutilus* L., and bream, *Abramis brama* L.) also increases (Jeppesen et al. 2000; Olin et al. 2002). Bachmann et al. (1996) observed gizzard shad to be absent in oligo- and mesotrophic lakes but were dominant species in eutrophic and hypereutrophic systems. The increased abundance of detritivorous species, coupled with increasing fish biomass, suggests the importance of fish assemblages in supporting algal production may increase with lake productivity (Vanni et al. 2006). However, the relative importance of fish as nutrient sources must be put into the context of other internal pathways (e.g., planktonic regeneration and loading from sediments) along a productivity gradient before the relevance of a single pathway can be determined. The capacity of any one source to support bacterial and algal production will vary interannually (Istvanovics et al. 2004; Shostell & Bukaveckas 2004), with lake productivity (Hudson et al. 1999; Sondergaard 2001), lake depth (Bostrom et al. 1988), and weather (Soranno et al. 1997). A comprehensive comparison of internal cycling of nutrients across systems and years may therefore advance our understanding of internal cycling of nutrients in lakes but, more importantly, also clarify the circumstances in which fish are important to nutrient cycling.

Model Limitations

Our models only account for the release of dissolved N and P, and do not measure the release of nutrients egested as faecal matter. As much as 40% of total regenerated N may be released as faeces (Porter et al. 1987; André et al. 2003). In addition, André et al. (2003) found that up to 50% of all P may be egested in particulate form. Nutrients egested as faeces may not be readily available to primary producers, and may settle out of the water column, representing a loss of nutrients from the epilimnion. Few studies have directly measured the release of nutrients in the form of faeces, and further research is warranted on the significance of egested nutrients in lakes.

The majority of fish nutrient release rates in our models were obtained from freshwater lakes. Therefore, our models should be applied to rivers and/or marine systems with extreme caution.

The importance of internal cycling of nutrients for supporting bacterial and primary production has been studied intensively (Kilham & Soltau-Kilham 1990; Hudson et al. 1999; Vanni et al. 2006; Zimmer et al. 2006). However, a comprehensive comparison of rates of nutrients supplied by each pathway along a trophic gradient of lakes has not been forthcoming. This probably reflects the difficulty in simultaneously estimating the contribution of multiple internal pathways. We have developed multi-species models to predict nutrient release (N and P) by fish assemblages. These models provide a useful addition to the empirical models of internal cycling of nutrients already available. These models incorporate direct measurements of release rates for a total of 56 marine and freshwater fish species, and capture the variation in release rates that may be attributable to fish mass, water temperature and feeding history (detritivore and non-detritivore).

Chapter 3: General Empirical Models for Predicting the Release of Nutrients by Aquatic Metazoans²

3.1. Introduction

Aquatic metazoans may regenerate mineral nutrients via their excretion and translocate them (i.e. benthic pelagic coupling) (Bayne & Scullard 1977; Urabe 1993; Wilhelm et al. 1999; Vander Zanden & Vadeboncoeur 2002; Vanni 2002; Andre et al. 2003). However, rates and ratios of nitrogen (N) and phosphorus (P) excreted are expected to vary within and across taxa. Alterations of food webs that lead to a change in the rate and/or stoichiometry of nutrients recycled may have direct implications for the abundance and composition primary producers. For example, a low ratio of N:P in the excretion of aquatic metazoans may favour the dominance of cyanobacteria (Schaus et al. 1997; Levine & Schindler 1999; Vanni 2002). While, inter- and intraspecific differences in rates and ratios of nutrients excreted by specific groups of metazoans have been studied (e.g. inter- and intraspecific differences of excretion by fish or zooplankton) (Wen & Peters 1994; Conroy et al. 2005; Torres & Vanni 2007), less is known about differences in excretion across a broader range of taxa (i.e. zooplankton vs. benthic macroinvertebrates vs. fish). Consequently, the significance of excretion across these taxa in determining rates and ratios of N and P regeneration in aquatic ecosystems is unclear.

The relative significance of nutrients supplied by different groups of metazoans (i.e., zooplankton vs. mussels vs. fish, or benthic vs. pelagic organisms) in supporting bacteria and algal productivity is expected to vary. For example, detritivorous fish excrete N and P at rates greater than non-detritivorous species (Sereda et al. 2008a). Similar differences might occur between other groups of benthic and pelagic feeding metazoans (e.g.,

² Contents of this chapter have been published in *Freshwater Biology*. 2011. **56**: 250-263.

zooplankton vs. benthic macroinvertebrates). However, taxonomic differences in rates and ratios of nutrients excreted have not been thoroughly investigated. This may reflect the difficulty in estimating simultaneously the rate of nutrient regeneration from several assemblages of metazoans.

An understanding of the significance of aquatic metazoans in nutrient pathways may be derived from empirical models (Wen & Peters 1994; Hudson & Taylor 2005; Sereda et al. 2008a) which provide the ability to estimate simultaneously rates and ratios of nutrient (N and P) release. The contribution of different groups of metazoans to the internal regeneration of nutrients can then be compared and assessed in relation to other nutrient fluxes (e.g. internal loading from the sediments and external loading from the catchment and atmosphere). Such comparisons may begin to provide a comprehensive understanding of the significance of any single pathway to the nutrient supply of aquatic ecosystems.

Direct measurement and bioenergetic modeling have been used to estimate rates of nutrient release by aquatic metazoans (Kraft 1992; Schindler et al. 1993; Conroy et al. 2005; Sereda et al. 2008b). While each method provides precise measurements of nutrient release, neither lends itself to the rapid estimation of nutrient release across systems. For example, knowledge of consumption and growth, plus the nutrient and energy content of both predators and prey are required for bioenergetic modeling (Kraft 1992). Moreover, direct measurements must be made several times over the season or year to capture the variation in rates due to changes in water temperature and feeding.

Rates of N and P release by individual organisms have been reported to be strongly correlated with organism mass (Wen & Peters 1994; Conroy et al. 2005; Sereda et al.

2008a), water temperature (Aldridge et al. 1995; Henry & Santos 2008; Sereda et al. 2008a) and diet (Anderson 1992; Schindler & Eby 1997). Empirical models that capture the variability in release rates attributable to these factors for a diversity of metazoan species may provide a means for predicting the release of nutrients and, therefore, may reduce the need for more complex and time-consuming approaches.

Our study had four overall objectives. First, to develop empirical models of N and P release as a function of organism mass and water temperature for several groups of aquatic metazoans (zooplankton, mussels, and benthic macroinvertebrates). Second, to compare intra- and inter-taxonomic differences in rates and ratios of nutrient excretion. Third, to determine if a single general model of N and P release for aquatic metazoans can be developed. Fourth, to apply our models to metazoan biomass and abundance data and to examine the influence of the relative abundance of different taxonomic groups on system-wide excretion rates.

3.2. Methods

We obtained directly measured nutrient release rates (N and P) for temperate and tropical, marine and freshwater aquatic organisms from lotic and lentic environments from the literature [zooplankton and benthic macroinvertebrates (Appendix 3.1)]. Rates were obtained for organisms from both field and laboratory studies. Studies where organisms were starved to obtain basal excretion rates were excluded from the analysis as these rates do not reflect natural conditions. We extracted release rates using data mining software (GetData Graph Digitizer v. 2.22, <http://get-data-graph-digitizer.com>) when information was presented only in plotted figures.

Organisms were subsequently divided into three broad categories; meso- and macrozooplankton, benthic macroinvertebrates other than molluscs (e.g., Amphipoda, Oligochaeta, Chironomidae, and Echinodermata) and molluscs. Zooplankton were further sub-divided into gelatinous (mainly Cnidaria, Ctenophora and Thaliacea) and non-gelatinous species, since gelatinous species have been reported to excrete N at rates much lower than other species (Jawed 1973; Schneider 1990; Wen & Peters 1994). Models of zooplankton excretion were developed for copepods and an “others” model for Cladocera, Mollusca, tunicates, euphausiids and Rotifera (as insufficient data was available for separate model development). Mussels were divided into 3 orders (Veneroida, Unionida, and Mytiloida) and into an “others” grouping encompassing the following orders: Nuculoida, Patellogastropoda, Ostreoida, Neotaenioglossa, and Mesogastropoda. Benthic macroinvertebrates were separated into the broad groups Diptera (i.e. Chironomidae) and an “others” group encompassing Amphipoda, Polychaetae, Annelida, Decapoda, Nematoda, and Turbellarians. Marine and freshwater organisms were modeled separately within each taxon to determine if marine and freshwater species release N and P at different rates. We also developed general models (e.g., all zooplankton or all mussels) to compare rates and ratios of nutrients across taxa (e.g. zooplankton vs. mussels vs. benthic macroinvertebrates). Models of N and P release by fish (Sereda et al. 2008a) have been included for comparison. We did not examine interspecific differences in excretion for fish as this has been thoroughly investigated elsewhere. For in depth analysis and discussion of interspecific difference in fish excretion refer to Gido (2002), Vanni et al. (2002), Higgins et al. (2006) and Torres & Vanni (2007).

Nutrient release rates that were presented only as mass-specific release rates ($\mu\text{g g}^{-1} \text{ h}^{-1}$), or as molar release rates ($\mu\text{mol h}^{-1}$), were converted to μg nutrients released $\text{h}^{-1} \text{ organism}^{-1}$. When release rates were presented as a function of organism wet mass, organism length or shell length (mussels), these measurements were converted to organism dry mass (shell free for mussels) using values reported by the study or with the use of conversion factors presented in the literature (Hirche 1983; James et al. 2001; Martin et al. 2006). Models of N and P release incorporate nutrients released in soluble form (e.g. NH_4 and PO_4) but do not account for nutrients released as faeces and pseudofaeces (mussels). A mean excretion rate and a mean dry mass were calculated for individual organisms when several individuals were measured in a single study. A mean excretion rate for each species was obtained from all other studies. General (all species combined) models were developed using species means. When a particular species spanned a broad range in body mass, a mean body mass and a mean excretion rate was calculated for a range in body mass (e.g. a mean for a species within 1–10 mg dry mass). This was done to preserve the allometric relationship between body mass and excretion rate for that species). Water temperature had a range of $-1.8\text{--}32^\circ\text{C}$ and dry mass had a range of 1×10^{-5} to 8×10^4 mg for all models.

We \log_{10} -transformed release rates and organism dry mass to normalize variance (Zar 1999). We then modeled nutrient release rates using multiple linear regression with individual organism dry mass and temperature as predictors. Tolerance (a measure of collinearity between independent variables) ranged from 0.57–1.0; however, interaction terms exhibited significant multicollinearity with both organism mass and water temperature (tolerances ranged from 0.02–0.35) and, therefore, we did not consider

second-order terms. We used Akaike's Information Criterion (AIC) to select the most parsimonious among candidate models (balancing simplicity and predictive power) containing the null (intercept only), single-predictor (either organism dry mass or temperature), and two-predictor equations (Burnham & Anderson 2004). AIC is defined as: $-2(\log\text{-likelihood}) + 2k$, where k is the number of estimable parameters of the model in question. We ranked models according to the distance in AIC units of each model relative to the best model ($\Delta\text{AIC} = \text{AIC}_i - \min \text{AIC}$, where AIC_i is the value for model i , and the $\min \text{AIC}$ is the value of the best model). Here, $\Delta\text{AIC} < 2$ gives support for a candidate model; whereas, ΔAIC values between 3 and 7 provide considerably less support, and $\Delta\text{AIC} > 10$ indicates that the model is improbable (Burnham & Anderson 2004).

We then compared the slope and intercept of models for marine and freshwater species within a taxon (e.g. zooplankton) [test of homogeneity of slope and intercept, Statistica (StatSoft, Inc., Tulsa, Oklahoma)] to determine if marine and freshwater species could be combined into a single model. We subsequently compared slopes and intercepts within and across taxa to determine intra- and inter-taxonomic differences in N and P excretion. Models were determined to be similar if slope and intercepts between models were non-significant ($p > 0.05$). Rates of nutrient release were then calculated by applying models to the range in organism dry mass encompassed by each model and to a water temperature of 20°C. Predicted rates of nutrients excreted and molar N:P ratios for each group of metazoans were then plotted as a function of organism dry mass for a visual comparison of taxonomic differences.

We obtained previously published biomass and abundance data for zooplankton, macroinvertebrates (Chaoboridae) and fish over a seven year period from two Canadian

Shield Lakes (Mouse and Ranger) located in south central Ontario, Canada (Demers et al. 2001; Ramcharan et al. 2001; Yan et al. 2001). Mouse and Ranger Lakes underwent a period of biomanipulation in the form of piscivore removal (McQueen et al. 2001) over which the relative abundance of fish, zooplankton and macroinvertebrates comprising total metazoan biomass changed (Demers et al. 2001; Ramcharan et al. 2001; Yan et al. 2001). As such, these lakes provide an ideal opportunity for understanding the influence of taxonomic differences in excretion on system wide rates of nutrient regeneration (i.e. how does the relative abundance of zooplankton, macroinvertebrates and fish influence rate of nutrient regeneration within aquatic environments?). Models were applied to previously collected biomass and abundance data for seven consecutive years (1991–1997) and assuming a constant water temperature of 20°C. Daily excretion rate ($\text{g ha}^{-1} \text{d}^{-1}$) and total metazoan biomass (kg ha^{-1}) were determined as the sum of excretion and biomass, respectively, for fish, zooplankton and macroinvertebrates. The percentage of total metazoan biomass (kg ha^{-1}) accounted for by each taxon (fish, zooplankton and macroinvertebrates) (e.g., $\text{kg ha}^{-1} \text{fish} / \text{kg ha}^{-1} \text{all metazoans}$) was determined for each of seven years. We then looked for relationships between total assemblage excretion rate ($\text{g ha}^{-1} \text{d}^{-1}$), total biomass (kg ha^{-1}) and the relative abundance of zooplankton, macroinvertebrates and fish (expressed as a percentage of total biomass). We also obtained rates of N and P excretion from published studies from temperate and tropical, marine and freshwater ecosystems. When rates were presented for several dates, a mean of all dates for the study were used. Mean water temperature was not available for all studies and, therefore, rates were not normalized to a constant temperature. We applied linear regression analysis to the data for each taxon to examine the inter-taxonomic

differences in assemblage excretion rates. Statistical analysis was performed with Statistica v. 6.1 (StatSoft, Inc., Tulsa, Oklahoma) and all significance levels were set at an alpha of 0.05.

3.3. Results

Models

The number of species incorporated into each model had a range of 9 to 74: zooplankton (74 and 52), mussels (23 and 9), benthic macroinvertebrates (25 and 11), and fish [45 and 42 (Sereda et al. 2008a)] for N and P models, respectively. The number of measurements incorporated into each individual model had a range of 40–1122 (Table 3.1). Freshwater organisms accounted for 8% and 18%, 47% and 100%, 42% and 78%, 18% and 0%, and 0% of the measurements in the zooplankton, mussels, other benthic macroinvertebrates and non-detritivorous and detritivorous fish N and P models, respectively.

We present only full additive models (i.e. intercept plus both organism dry mass and water temperature as predictors, Table 3.1) based on model selection using AIC. The full models (dry mass and water temperature) for predicting N release were superior to the next-best model by at least 1146 AIC units ($1146 - 1.96 \times 10^{262}$). The full models for organism P release (organism dry mass and water temperature) were superior to the next-best model by at least 1.44×10^9 AIC units ($1.44 \times 10^9 - 9.1 \times 10^{165}$).

Table 3.1. Empirical models for predicting the release of nutrients (N and P) by zooplankton, mussels, benthic macroinvertebrates and fish as a function of the logarithm of organism dry mass (mg) and mean water temperature (°C). Multiple regression models were developed from direct measurements of the rate of nutrient release reported in the literature. The number of different species in each model ranged from 11–74. Model selection was conducted with AIC. The partial correlations (R) are shown. Note that the nutrient release models for fish are derived from Sereda et al. (2008a) but are presented here (for comparison) as a function of organism dry mass.

Model	Coefficient	SE	<i>t</i> -statistic	<i>p</i> -value	<i>R</i>
Nitrogen					
<i>General Zooplankton</i> ($n = 282$, $R^2 = 0.78$, $p < 0.001$)					
Intercept	-1.106	0.057	-19.44	<0.001	
Log dry mass (mg)	0.622	0.023	28.49	<0.001	0.86
Temperature (°C)	0.029	0.004	7.00	<0.001	0.37
<i>Copepods</i> ($n = 98$, $R^2 = 0.58$, $p < 0.001$)					
Intercept	-1.161	0.045	-25.61	<0.001	
Log dry mass (mg)	0.370	0.035	10.60	<0.001	0.74
Temperature (°C)	0.016	0.003	5.60	<0.001	0.50
<i>“Other” Zooplankton</i> ($n = 406$, $R^2 = 0.66$, $p < 0.001$)					
Intercept	-1.366	0.043	-31.88	<0.001	
Log dry mass (mg)	0.775	0.024	31.85	<0.001	0.85
Temperature (°C)	0.061	0.005	11.96	<0.001	0.51
<i>General Mussels</i> ($n = 361$, $R^2 = 0.73$, $p < 0.001$)					
Intercept	-3.684	0.166	-22.18	<0.001	
Log dry mass (mg)	1.238	0.043	28.53	<0.001	0.83
Temperature (°C)	0.084	0.006	13.47	<0.001	0.58

Veneroida ($n = 322$, $R^2 = 0.82$, $p < 0.001$)

Intercept	-1.087	0.299	-3.64	<0.001	
Log dry mass (mg)	0.897	0.027	33.02	<0.001	0.89
Temperature (°C)	-0.027	0.013	-2.17	0.03	0.12

Unionida ($n = 150$, $R^2 = 0.27$, $p < 0.001$)

Intercept	-3.456	1.118	-3.09	0.002	
Log dry mass (mg)	1.886	0.265	7.12	<0.001	0.51
Temperature (°C)	-0.035	0.029	-1.22	0.23	-0.10

Mytiloida ($n = 84$, $R^2 = 0.91$, $p < 0.001$)

Intercept	-4.721	0.266	-17.75	<0.001	
Log dry mass (mg)	1.128	0.073	15.50	<0.001	0.86
Temperature (°C)	0.163	0.006	27.25	<0.001	0.95

“Other” Mussels ($n = 218$, $R^2 = 0.85$, $p < 0.001$)

Intercept	-3.126	0.085	-36.68	<0.001	
Log dry mass (mg)	0.973	0.034	28.54	<0.001	0.89
Temperature (°C)	0.077	0.004	18.36	<0.001	0.78

General Benthic Macroinvertebrates ($n = 144$, $R^2 = 0.87$, $p < 0.001$)

Intercept	-0.254	0.166	-1.53	0.13	
Log dry mass (mg)	0.960	0.032	29.72	<0.001	0.93
Temperature (°C)	0.012	0.008	1.50	0.14	0.13

General Non-detritivorous Fish ($n = 261$, $R^2 = 0.92$, $p < 0.001$)

Intercept	-1.448	0.156	-9.31	<0.001	
Log dry mass (mg)	0.884	0.017	51.53	<0.001	1.00

Temperature (°C)	0.033	0.005	7.11	<0.001	0.14
<i>General Non-detritivorous Fish and Zooplankton</i> ($n = 1122$, $R^2 = 0.81$, $p < 0.001$)					
Intercept	-1.341	0.041	-32.90	<0.001	
Log dry mass (mg)	0.763	0.011	63.9	<0.001	0.86
Temperature (°C)	0.022	0.002	10.27	<0.001	0.14
<i>General Detritivorous Fish</i> ($n = 371$, $r^2 = 0.79$, $p < 0.001$)					
Intercept	0.116	0.095	1.21	0.22	
Log dry mass (mg)	0.728	0.021	34.22	<0.001	0.86
Temperature (°C)	0.012	0.003	3.64	<0.001	0.09
Phosphorus					
<i>General Zooplankton</i> ($n = 190$, $R^2 = 0.96$, $p < 0.001$)					
Intercept	-1.631	0.033	-49.76	<0.001	
Log dry mass (mg)	0.654	0.009	67.04	<0.001	0.98
Temperature (°C)	0.029	0.002	14.88	<0.001	0.74
<i>Copepods</i> ($n = 63$, $R^2 = 0.86$, $p < 0.001$)					
Intercept	-1.677	0.041	-41.34	<0.001	
Log dry mass (mg)	0.926	0.064	14.48	<0.001	0.88
Temperature (°C)	0.033	0.002	15.64	<0.001	0.89
<i>“Other” Zooplankton</i> ($n = 595$, $R^2 = 0.95$, $p < 0.001$)					
Intercept	-1.722	0.019	-91.12	<0.001	
Log dry mass (mg)	0.674	0.007	102.86	<0.001	0.97
Temperature (°C)	0.031	0.001	22.79	<0.001	0.68

Mussels – Veneroida ($n = 106$, $R^2 = 0.68$, $p < 0.001$)

Intercept	-4.399	0.305	-14.44	<0.001	
Log dry mass (mg)	0.444	0.032	13.82	<0.001	0.81
Temperature (°C)	0.131	0.013	9.60	<0.001	0.69

Unionida ($n = 178$, $R^2 = 0.02$, $p = 0.13$)

Intercept	1.449	0.703	2.06	0.04	
Log dry mass (mg)	-0.049	0.166	-0.29	0.77	-0.02
Temperature (°C)	-0.031	0.015	-2.04	0.04	-0.15

General Benthic Macroinvertebrates ($n = 40$, $R^2 = 0.31$, $p < 0.001$)

Intercept	-0.650	0.259	-2.51	0.02	
Log dry mass (mg)	0.126	0.032	3.88	0.0004	0.54
Temperature (°C)	0.027	0.013	2.06	0.04	0.32

General Non-detritivorous Fish ($n = 188$, $R^2 = 0.82$, $p < 0.001$)

Intercept	-1.352	0.169	-7.99	<0.001	
Log dry mass (mg)	0.733	0.026	28.58	<0.001	0.90
Temperature (°C)	0.013	0.006	2.19	0.03	0.07

General Non-detritivorous Fish and Zooplankton ($n = 854$, $R^2 = 0.97$, $p < 0.001$)

Intercept	-1.734	0.016	-106.26	<0.001	
Log dry mass (mg)	0.690	0.005	151.20	<0.001	0.94
Temperature (°C)	0.033	0.001	35.16	<0.001	0.22

General Detritivorous Fish ($n = 384$, $R^2 = 0.88$, $p < 0.001$)

Intercept	-0.887	0.078	-11.32	<0.001	
Log dry mass (mg)	0.769	0.015	50.84	<0.001	0.92

Temperature (°C)	0.012	0.003	3.87	<0.001	0.07
------------------	-------	-------	------	--------	------

Significant positive correlations ($P \leq 0.001$) between the logarithm of organism dry mass, water temperature and the logarithm of nutrient release rate was observed for each model (Table 3.1). The logarithm of organism dry mass explained 51–93% (partial correlation, R) of the logarithm of N release (Table 3.1); whereas, water temperature explained 9–95%. The logarithm of organism dry mass explained 54–98% (partial correlation, R) of the logarithm of P release (Table 3.1), whereas water temperature explained 7–74%.

Intra-taxonomic Differences in Excretion

Zooplankton

Slopes and intercepts of N models for copepods and other zooplankton were significantly different ($p < 0.001$). Copepods released N (as a function of dry mass) more slowly than other zooplankton (Table 3.1). Sufficient data were not available to compare rates of N excretion between marine and freshwater zooplankton.

Slopes and intercepts of P models for copepods and other zooplankton were significantly different ($p < 0.001$) (Table 3.1). Copepods released P (as a function of dry mass) faster than other zooplankton (Table 3.1). Slopes and intercepts of models of zooplankton excretion developed for marine and freshwater species were not significantly different ($p \geq 0.06$).

Mussels

Slope and intercepts of N excretion models were significantly different between mussel orders ($p < 0.001$) (Table 3.1). Rates of N excretion scaled less than

proportionally with dry mass (slope <1) for the Veneroida whereas N excretion scaled proportionally (slope ~ 1) and greater than proportionally (slope >1) with organism dry mass for “other” mussel orders, the Unionida and for all mussels combined (i.e. the general model), respectively. The relationship between N excretion and organism dry mass and water temperature for unionids was weak ($R^2 = 0.27$) and the effect of temperature on excretion rate was non-significant ($p = 0.23$). Slopes and intercepts of N excretion models for marine and freshwater mussels were not significantly different ($p \geq 0.07$).

Rates of P excretion were significantly different between mussel orders ($p \leq 0.007$). A significant positive relationship between the logarithm of organism dry mass, water temperature and the logarithm of P excretion was observed for veneroid mussels ($n = 106$, $R^2 = 0.68$, $p < 0.001$) (Table 3.1). However, a relationship between the logarithm of organism dry mass, water temperature and the logarithm of P release was not observed for unionids ($n = 178$, $R^2 = 0.02$, $p = 0.13$) (Table 3.1). A general model (all orders combined) was not developed because of clear (visual) separation in release rates between veneroids and unionids. Phosphorus excretion rates were not available for marine species and, therefore, a comparison between freshwater and marine species was not possible.

Benthic Macroinvertebrates

Slopes and intercepts for models of N excretion across orders of benthic macroinvertebrates and/or for marine and freshwater species were not significantly different ($p \geq 0.05$). Therefore, a single general model of N excretion by benthic

macroinvertebrates was developed (Table 3.1). Rates of N excretion scaled proportionally with organism dry mass (slope ~ 1).

A weak positive relationship between organism dry mass, water temperature and rate of P excretion was observed (Table 3.1). Data were insufficient to compare rates of P excretion between marine and freshwater species.

Inter-taxonomic Differences in Excretion

Slopes and intercepts were significantly different between N models when all models were compared (test of slope and intercept, $p \leq 0.001$). Therefore, N models were not combined into a single general model. Therefore, we performed multiple pair-wise comparisons (applying Bonferroni corrections) to determine if any two or three models could be combined. We determined that the slopes and intercepts of N-release models between the general zooplankton and non-detritivorous fish were not significantly different ($p \geq 0.16$) and thus were combined into a single general model (Table 3.1, Fig. 3.1a).

Slopes and intercepts were significantly different between general models of P release when all models were considered ($p \leq 0.001$). Therefore, models of P release were not combined into a single general model. However, slopes and intercepts between the general zooplankton and non-detritivorous fish models of P release were not significantly different ($p \geq 0.44$) and thus were combined into a single general model (Table 3.1, Fig. 3.1b).

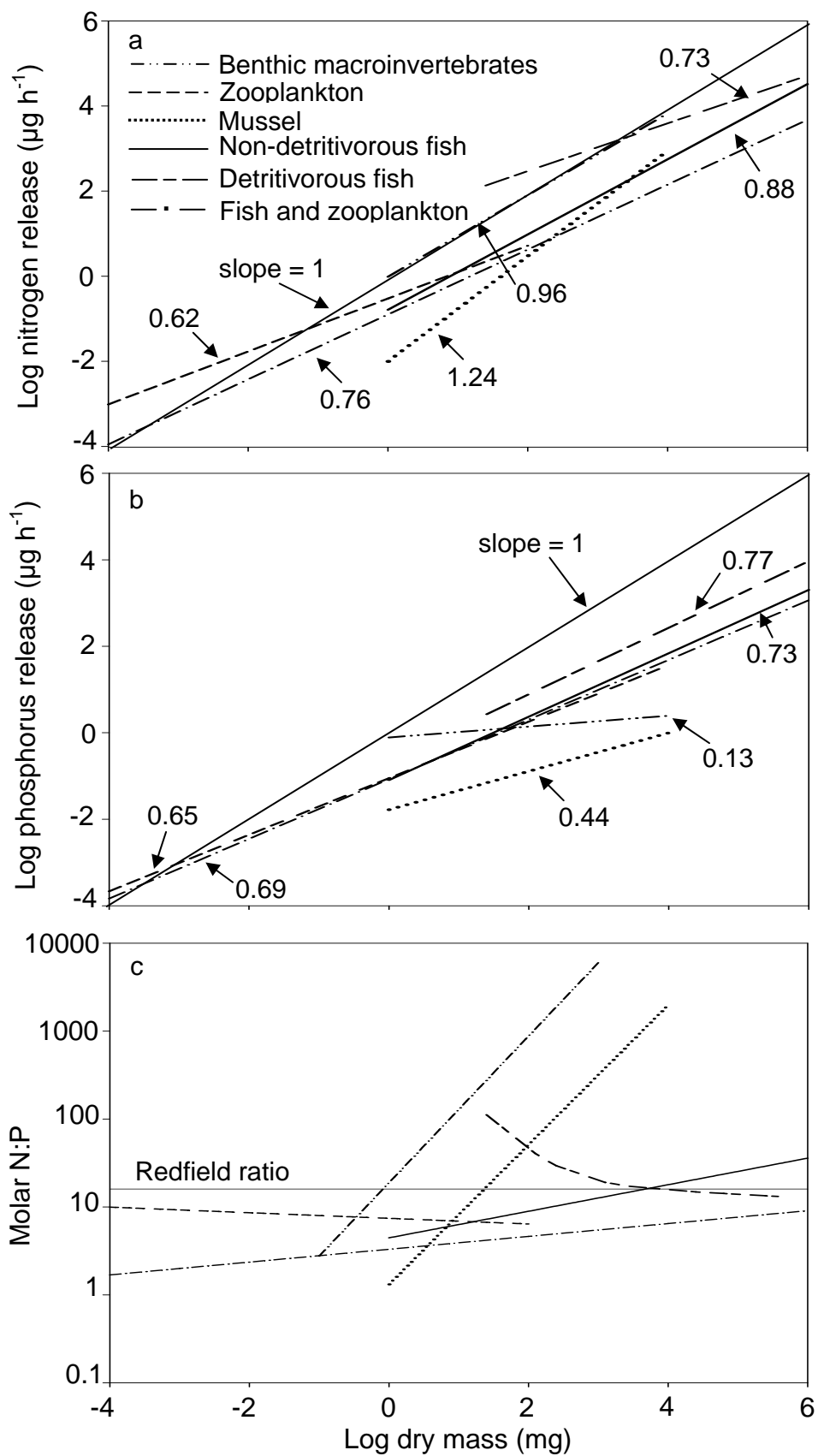


Figure 3.1. Rates of nitrogen (a) and phosphorus release (b) ($\mu\text{g h}^{-1}$) and molar N:P ratios predicted by the empirical models (c). Models were applied to the range of organism dry mass (mg) encompassed by each model and to a temperature of 20°C. The Redfield N:P ratio of 16:1 is shown for comparison. Also shown in a) and b) are the slopes (linear regression) for each taxon. Note that detritivorous fish excrete both N and P at rates greater than for other metazoans. Molar ratio of N and P excreted by zooplankton and detritivorous fish decline with increasing organism mass (c) whereas N:P ratios increase with increasing dry mass for all other metazoans. Note that mussel N:P ratios were calculated for Veneroida only.

Rates of nitrogen excretion scaled less than proportionally with organism dry mass for each taxon (i.e. mass coefficients <1 , Table 3.1) (Fig. 3.1a), except for mussels, in which excretion rate increased with organism dry mass (slope = 1.238, Table 3.1). Detritivorous fish excreted N at a greater rate than any other aquatic metazoans (Table 3.1, Fig. 3.1a). Benthic macroinvertebrates excreted N at a greater rate than either zooplankton or fish across the full range of organism dry mass (Fig. 3.1a). Mussels generally excreted N at the lowest rate, but exceeded rates of N excretion by zooplankton and fish when larger mussels were considered (Fig. 3.1a).

Rates of P excretion scaled less than proportionally with organism dry mass for each taxon (i.e., mass coefficients <1 , Table 3.1) (Fig. 3.1b). Detritivorous fish excreted P at rates greater than all other aquatic metazoans. Benthic macroinvertebrates generally excreted P more quickly than other taxa (Fig. 3.1b) whereas mussels excreted P at a rate less than any other metazoans.

Molar N:P ratios had a range of 6.4–9.9, 1.3–1978, 2.8–5987, 4.5–35.9 and 13–111 for zooplankton, mussels, benthic macroinvertebrates and non-detritivorous and detritivorous fish, respectively (Fig. 3.1c). Note that mussel N:P ratios were calculated for veneroid mussels only, whereas all other N:P ratios were calculated using the general models. Molar N:P ratios increased with increasing organism dry mass, except for

zooplankton and detritivorous fish, where N:P ratios declined with increasing dry mass (Fig. 3.1c). N:P ratios generally were less than the Redfield ratio of 16:1; however, the ratios of nutrients excreted depended on organism size.

Assemblage excretion rates

We applied our models to previously collected biomass and abundance data for zooplankton, macroinvertebrates (Chaoboridae) and fish over a seven year period from Mouse and Ranger Lakes. Over the seven year period the relative abundance of fish, zooplankton and macroinvertebrates comprising total metazoan biomass had changed (Demers et al. 2001; Ramcharan et al. 2001; Yan et al. 2001), providing the ideal opportunity to understand the how the relative abundance of zooplankton, macroinvertebrates and fish influence rates of nutrient regeneration within aquatic ecosystems. Nitrogen and P excretion increased linearly with assemblage biomass ($R^2 \geq 0.82, 0.95$ and 0.90 , for zooplankton, macroinvertebrates and fish, respectively). Rates of N and P excretion by mixed assemblages (all metazoans combined) increased linearly with increasing total biomass (Fig. 3.2). However, the abundance of fish (expressed as a percentage of total metazoan biomass) was significantly and negatively correlated with rates of N and P excretion ($R \geq -0.55, p \leq 0.04$) whereas the abundance of zooplankton was positively correlated with the rate of total N and P excretion ($R \geq 0.57, p \leq 0.03$). A relationship between the abundance of macroinvertebrates and N excretion was not detected. Phosphorus excretion was not estimated for macroinvertebrates because our models do not include rates of P excretion for chaoborids. Biomass and abundance data for mussels were not available for a similar analysis.

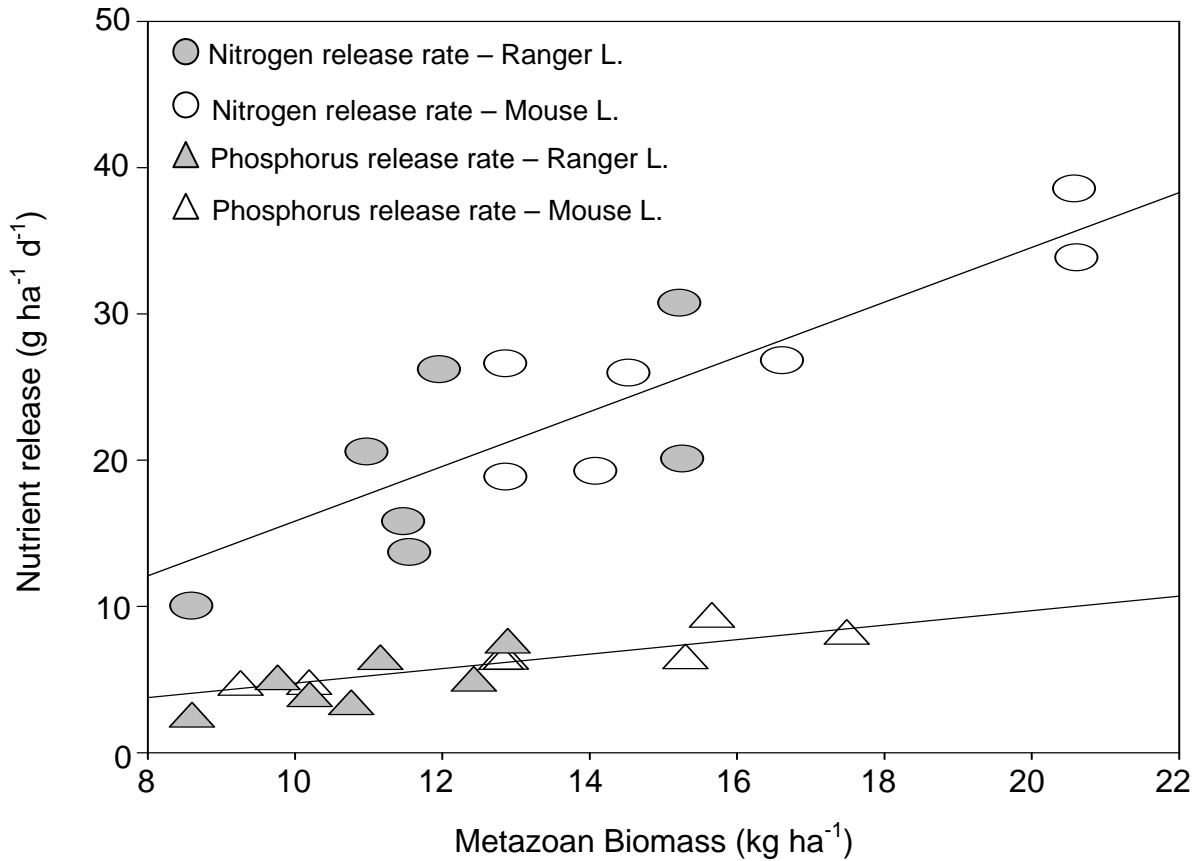


Figure 3.2. Rates of nitrogen and phosphorus excretion ($\text{g ha}^{-1} \text{d}^{-1}$) as a function of metazoan biomass (fish, zooplankton and macroinvertebrates) (kg ha^{-1}) in Mouse and Ranger Lakes. Models were applied to the biomass and abundance data in each lake over a 7 year period (1991–1997). Water temperature was held constant at 20°C . Note, that N and P excretion increases linearly with assemblage biomass.

We also obtained rates of N and P excretion from published studies from temperate and tropical, marine and freshwater ecosystems. Rates of N and P excretion of assemblages of aquatic metazoans increased linearly with increasing biomass (Table 3.2, Fig. 3.3a, b). Rates of N and P excretion by metazoans generally overlapped; however, rates of excretion by zooplankton, mussels and benthic macroinvertebrate assemblages were greater than rates for fish for a given assemblage biomass (Table 3.2, Fig. 3.3a, b).

Table 3.2. Linear regression coefficients for rates of N and P excretion by metazoan assemblages obtained from published studies. Coefficients correspond to regressions presented in Fig 3.3.

	Coefficient	SE	<i>t</i> -statistic	<i>p</i> -value
Nitrogen				
<i>Zooplankton</i> ($n = 11$, $R^2 = 0.93$, $p < 0.001$)				
Intercept	-0.254	0.192	-1.32	0.22
Log dry mass (mg)	1.601	0.143	11.16	<0.001
<i>Mussels</i> ($n = 98$, $R^2 = 0.58$, $p < 0.001$)				
Intercept	1.135	0.761	1.49	0.16
Log dry mass (mg)	0.704	0.222	3.17	0.009
<i>Benthic Macroinvertebrates</i> ($n = 10$, $R^2 = 0.22$, $p = 0.17$)				
Intercept	1.176	0.581	2.02	0.08
Log dry mass (mg)	0.405	0.268	1.51	0.17
<i>Fish</i> ($n = 71$, $R^2 = 0.87$, $p < 0.001$)				
Intercept	-0.690	0.112	-6.19	<0.001
Log dry mass (mg)	1.187	0.056	21.39	<0.001
Phosphorus				
<i>Zooplankton</i> ($n = 6$, $R^2 = 0.39$, $p = 0.39$)				
Intercept	0.906	0.466	1.94	0.11
Log dry mass (mg)	0.384	0.410	0.94	0.39
<i>Mussels</i> ($n = 9$, $R^2 = 0.80$, $p < 0.001$)				
Intercept	-0.797	0.639	-1.25	0.25

Log dry mass (mg)	1.037	0.199	5.20	<0.001
<i>Fish</i> ($n = 89$, $R^2 = 0.83$, $p < 0.001$)				
Intercept	-0.792	0.058	-13.70	<0.001
Log dry mass (mg)	0.952	0.043	22.33	<0.001

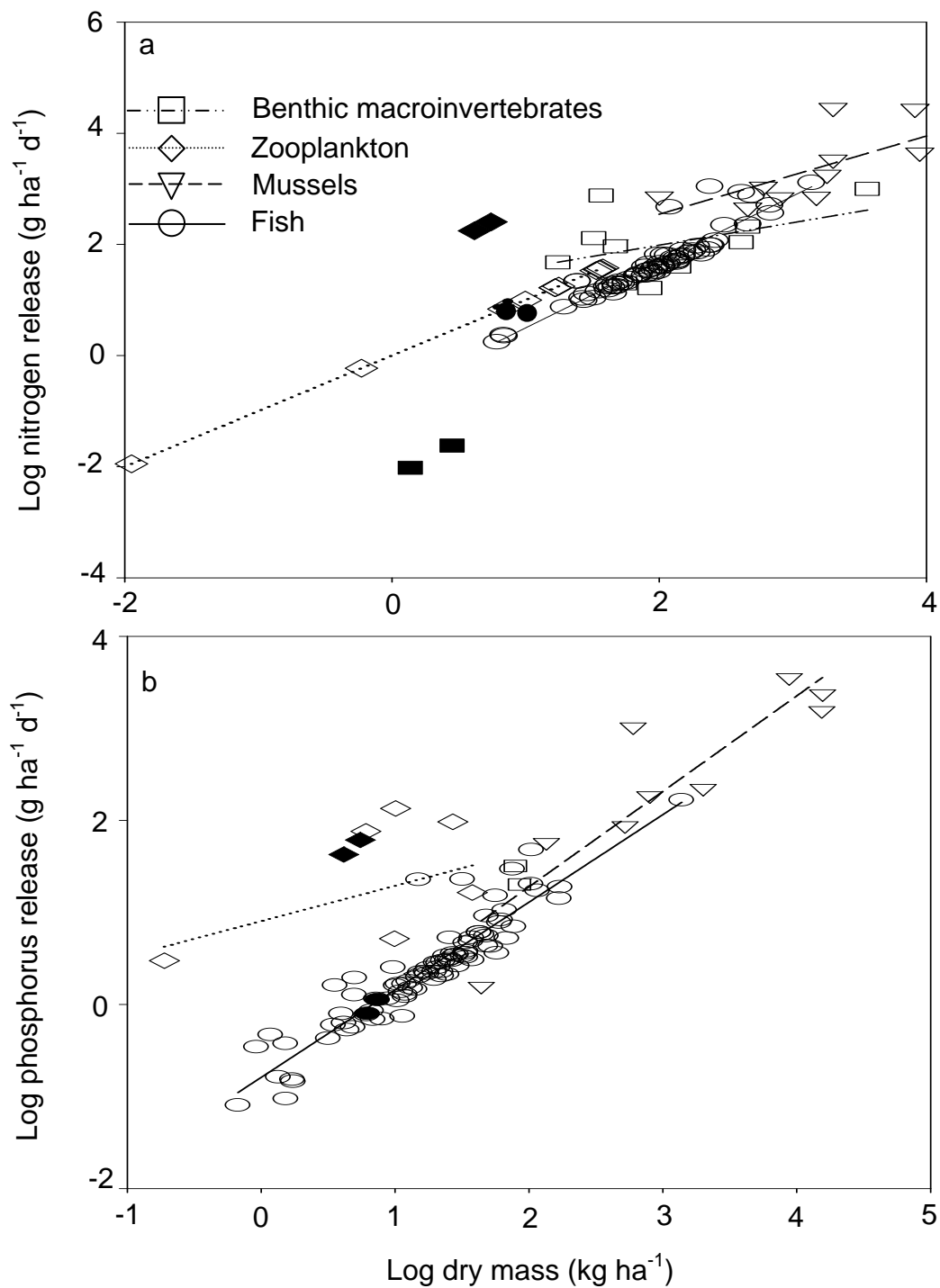


Figure 3.3. Rates of nitrogen (a) and phosphorus (b) excretion ($\text{g ha}^{-1} \text{d}^{-1}$) by aquatic metazoans as a function of assemblage biomass (kg ha^{-1}). Rates were obtained from the literature for marine and freshwater, temperate and tropical systems [fish (Nixon et al. 1976; Horppila 1998; Brabrand et al. 1990; Boers et al. 1991; Schindler et al. 1993; Persson 1997; Gido 2002; Griffiths 2006; Sereda et al. 2008a); benthic macroinvertebrates (Needham 1957; Nixon et al. 1976; Gardner et al. 1981; Madeira et

al. 1982; Smith 1983; Gray 1985; Starkel 1985; Grimm 1988; Fukuhara & Yasuda 1989; Nithart et al. 1999; Henry & Santos 2008); zooplankton (Barlow & Bishop 1965; Hargrave & Geen 1968; Jawed 1973; Peters 1975; Bartell 1981; Park & Carpenter 1987; Pinto-Coelho & Greco 1999; Atkinson & Whitehouse 2001; Hernandez-Leon & Ikeda 2005); mussels (Jordan & Valiela 1982; Prosch & McLachlan 1984; Nalepa et al. 1991; Prins & Smaal 1994; Mellina et al. 1995; Ozersky et al. 2009). Regression coefficients for each taxon are presented in Table 1. Note that a regression line is not available for benthic macroinvertebrate P release as only two data points are present. Also note that solid symbols correspond to the same taxa as in the legend, but excretion rates represent mean values of taxon calculated for metazoans in Mouse and Ranger Lakes using our general models.

3.4. Discussion

Models

Here we focus on the new models developed (for zooplankton, mussels and benthic macroinvertebrates). For a detailed discussion on the empirical models of nutrient release by fish refer to Sereda et al. (2008a).

Wen and Peters (1994) presented a comprehensive set of empirical models for predicting the release of nutrients by meso- and macrozooplankton (i.e. predicting the release of N and P as a function of organism dry mass). However, these models provided only moderate predictive power, and multivariate models that include water temperature as an explanatory variable may improve model accuracy. Our general models for zooplankton incorporated 190 and 63 measurements of nutrient release, explaining 78% and 96% of the variance in N and P release, respectively (Table 3.1). The variance explained by our multivariate model (organism dry mass and temperature) of N release by zooplankton ($R^2 = 0.78$) was only a marginal improvement over that explained by the bivariate model (organism dry mass) of Wen and Peters (1994) ($n = 574$, $R^2 = 0.72$). However, our multivariate model of P release by zooplankton explained substantially more of the variance in P release ($R^2 = 0.96$) than the model of Wen and Peters (1994) (n

= 462, $R^2 = 0.63$). Moreover, water temperature alone, explained 37 and 74% (partial correlations) of the variation in N and P release, respectively (Table 3.1). Evidently, inclusion of water temperature as a predictive variable improves model accuracy.

The lack of difference in excretion rates between orders of benthic macroinvertebrates was unexpected, as interspecific differences in N excretion for benthic invertebrates have been observed (Alves et al. 2010). Our inability to detect differences in excretion between orders of benthic macroinvertebrates may reflect the limited data (i.e. only comparing two orders, Diptera and “others”). Nevertheless, our model provides the ability to estimate N excretion from benthic macroinvertebrates and provides a basis for future models reserved for more taxa.

Our model of P release for benthic macroinvertebrates explained only 31% of the variance. Despite our P model incorporating rates of P release for 11 species, the majority of measurements were obtained from a single study (Henry & Santos 2008) for a single family (Chironomidae). Furthermore, the dry mass of the organisms in the model spanned only a very narrow range of dry mass (0.05–35.2 mg). Consequently, more data are required to model accurately rates of P release by benthic macroinvertebrates. However, we advocate the development of such a model because of the potential significance of benthic macroinvertebrates to the nutrient flux in lakes. For example, rates of P excretion by amphipods in the fishless Snowflake Lake were five–17 times greater (Wilhelm et al. 1999) than rates of P regeneration by fish in a set of alpine lakes (Schindler et al. 2001). Consequently, an ability to predict rates of nutrient release by benthic macroinvertebrates is essential for a comprehensive understanding of nutrient flux in lakes.

Mussels from different taxonomic orders excreted N and P at significantly different rates (Table 3.1). The significance of this variation may be particularly evident in systems where a particular order of mussel is dominant. For example, the shell free biomass of the invasive zebra mussel (*Dreissena polymorpha* Palls) (Order Veneroida) in Lake St. Clair is up to 119 mg m^{-2} , a mass four times greater than all other benthic invertebrates combined (Nalepa et al. 1991). Zebra mussels excrete N:P at ratios below Redfield (Arnott & Vanni 1996), possibly inducing N limitation and favouring N-fixing cyanobacteria. An increase in toxic cyanobacteria (e.g. *Microcystis aeruginosa* Kutzinger) has been associated with an increase in the biomass of zebra mussels (Vanderploeg et al. 2001; Raikow et al. 2004). Excretion at low N:P ratios (Arnott & Vanni 1996) may explain this observation. Nonetheless, the broad range of excretion rates across mussel taxa suggests that intra-taxon differences in excretion should be considered when estimating excretion rates and ratios for mussel assemblages.

Temperature had a greater effect on the rates of N and P release for mussels than for other aquatic organisms (temperature coefficients of 0.08 and 0.13 for N and P in general models, respectively, Table 3.1). Aldridge et al. (1995) also reported a significant effect of temperature on ammonia excretion with rates in zebra mussels increasing by a factor of ~five over a 12°C temperature increase. As sedentary benthic organisms, mussels may experience relatively isothermal conditions relative to organisms that undergo diel vertical migrations. Consequently, mussels may not have the physiological adaptations required for regulating metabolic rates. For example, Fukuhara and Yasuda (1989) suggested that low values of Q_{10} observed in chaoborids (~1.6) may indicate a

physiological adaptation to temperature extremes while undergoing diel vertical migrations.

Inter-taxon Comparison of Release Rates and Ratios

There was substantial overlap in rates of N release as a function of organism dry mass across taxa (Fig. 3.1a). However, detritivorous fish excreted N at rates substantially greater than other metazoans. Consequently, detritivorous species may have a disproportionate influence on N regeneration in aquatic ecosystems. For example, Sereda et al. (2008a) demonstrated that a single species (gizzard shad, *Dorosoma cepedianum* Lesueur) could increase rates of N excretion by <1-331% when feeding as a detritivore rather than a planktivore. Interestingly, a substantial separation between other benthic and pelagic organisms (i.e. between zooplankton, mussels, benthic macroinvertebrates and non-detritivorous fish) was not observed (Fig. 3.1a). High rates of nutrient excretion have been associated with an increased rate of consumption (Durbin & Durbin 1981; Ramnarine et al. 1987). However, the greater rate of N excretion for detritivorous fish is largely associated with a higher intercept, as the slope of the regression is intermediate relative to other metazoans (Fig. 3.2a). Gizzard shad undergo ontogenetic diet shifts, feeding on zooplankton as larvae and detritus as juveniles and adults (Pilati & Vanni 2007). The N content of zooplankton (~10% by mass) is much greater than the ambient N content of sediment detritus (~0.18%) (Higgins et al. 2006). We assumed the diet of the gizzard shad was solely detritus (based on observations in respective studies), however, an overlap in diet for these smaller fish (i.e. consumption of zooplankton and detritus) may result in the consumption of N in excess of metabolic demand resulting in greater rates of N excretion than either juveniles or adults.

There was greater separation in P excretion rates between taxa (Fig. 3.1b). However, consistent with N excretion, detritivorous fish excreted P at rates greater than other metazoans whereas mussels excreted P more slowly than other taxa. The release of soluble reactive phosphorus from iron complexes in the ingested sediments may explain the large amounts of P released by detritivorous fish (Brabrand et al. 1990).

Rates of excretion by mixed assemblages of metazoans increased linearly with assemblage biomass (Figs 3.2 & 3.3). However, the relative abundance of different taxa (i.e. zooplankton, mussels, benthic macroinvertebrates or fish) may determine the rate of increase in excretion. For example, the abundance of fish (expressed as a percentage of total metazoan biomass) was negatively correlated with total N and P excretion whereas the abundance of zooplankton was positively correlated. This probably reflects the role of planktivorous fish in reducing the abundance of zooplankton which exhibit a greater mass specific excretion rate. It has been demonstrated that the biomass of metazoans (e.g. zooplankton, mussels, benthic macroinvertebrates and fish) increases linearly along a trophic gradient in lakes (i.e. biomass increases with increasing total P) (Hanson & Leggett 1982; Hanson & Peters 1984; Wilson & Sarnelle 2002; Griffiths 2006). As such, total nutrient regeneration by aquatic metazoans is expected also to increase. However, the rate of increase in nutrient regeneration will depend on how the abundances of zooplankton, mussels, benthic macroinvertebrates and fish change relative to one another along the trophic gradient. Moreover, the relative contribution of different groups of metazoans to the nutrient supply for primary producers will depend on whether the nutrients are recycled within the water column (e.g. zooplankton excretion), or represent

a transfer of nutrients into the epilimnion through benthic pelagic coupling (e.g. through vertical migrations of benthic feeding invertebrates or fish).

Excretion of nutrients at N:P ratio below the Redfield ratio may favour the dominance of cyanobacteria (Schaus et al. 1997; Levine & Schindler 1999; Vanni 2002). Therefore, it is of interest to understand how the ratio of N:P excreted may vary with organism size and across taxa. Zooplankton and benthic macroinvertebrates excreted N:P at ratios below Redfield across the full range in organism dry mass. On the other hand, mussels, non-detritivorous and detritivorous fish excreted N:P at ratios either greater than or less than 16:1, depending on the mass of the organism (Fig. 3.1c). As such, the potential of metazoans to influence nutrient stoichiometry will depend on the size structure of the assemblage and on the dominance of a particular taxon (e.g. a system in which metazoan biomass is dominated by zooplankton may have N:P ratios less than a system in which biomass is dominated by fish). For example, the mean ratios of N:P excreted by fish was 18.4 and 20.6 for Mouse and Ranger Lakes, respectively. In contrast, the ratio of N:P excreted by zooplankton was 9.2 in both Mouse and Ranger Lakes. However, mean N:P ratios of 9.3 and 9.4 were calculated for the combined assemblage of zooplankton and fish in Mouse and Ranger Lakes, respectively. Consequently, when mixed assemblages were considered, N:P ratios approximated the ratio excreted by zooplankton. This may reflect the greater contribution of zooplankton (relative to fish) to total nutrient regeneration.

Model Limitations

Models of N and P release did not account for nutrients released as faeces and pseudofaeces (mussels). Nutrients egested in these ways may represent a significant flux

of N and P into the sediments. For example, over 50% of the P filtered by the mussel population in Lake St. Clair was released as faeces and pseudofaeces (~134 MT) (Nalepa et al. 1991). However, Jordan & Valiela (1982) reported that the population of ribbed mussels (*Geukensia demissa* Dillwyn) in a New England salt marsh deposited ~1264 kg of particulate N. Although, nutrients egested in particulate form are not available for immediate uptake, the development of models for predicting rates of egested nutrients would advance our ability to estimate rates of nutrient flux in aquatic ecosystems.

It has been suggested that ecological stoichiometry offers a framework for predicting how animal species vary in recycling nutrients (Vanni et al. 2002). Stoichiometric theory predicts that under homeostatic conditions N:P excreted should be negatively correlated with body N:P and positively correlated with food N:P (Sternner et al. 1992). While some evidence has been found for the relationship between body N:P and N:P excreted (Vanni et al. 2002), the results have been inconsistent (Torres & Vanni 2007; Alves et al. 2010). Moreover, several studies have suggested that N:P of food has a greater influence over the variation in excretion rate and ratio than does body N:P (Elser & Urabe 1999; Pilati & Vanni 2007; Torres & Vanni 2007). Although we do not have adequate data to place our models in a stoichiometric framework (i.e. we do not have data on body N:P or food N:P for all organisms) such an analysis in a future study is warranted. We assumed that variation in diet may be captured in our models through the inclusion of many species from a diverse set of habitats; however, we can not quantify its significance. Therefore, inclusion of stoichiometric variation (food and consumer body N:P) as a variable in our models is likely to increase the amount variance in excretion rates explained within and across taxa.

Larval organisms were underrepresented in our models. This probably reflects the difficulty of obtaining direct measurements of N and P excretion for this size class. Nonetheless, N and P excretion by larval organisms (particularly fish) may represent a substantial source of nutrients for primary producers. For example, Kraft (1992) estimated that over half of the P regenerated by the alewife (*Alosa pseudoharengus* Wilson) in Lake Michigan was produced by larvae and age-0 fish. Furthermore, the stoichiometry of nutrients excreted by larval fish (i.e. N:P ratio) may be significantly different from juvenile and adults. For example, larval gizzard shad excrete N and P at ratios higher than both juveniles and adults (Pilati & Vanni 2007) (also see Fig. 3.1c). This difference in N:P ratio of excretions is attributed to ontogenetic diet shifts from zooplankton (N:P composition of ~25:1; Sterner & Elser 2002) to sediment detritus (N:P composition of ~12:1; Higgins et al. 2006). A similar shift in the stoichiometry of nutrients excreted may be observed in other organisms, particularly within zooplankton or benthic invertebrates assemblages that shift habitat and/or diet in the presence or absence of fish.

Finally, the use of log-log relationships in developing our models may hide a substantial amount of unexplained variation. Our models may be applied to metazoan biomass and abundance to estimate excretion rates, but they should be applied with caution where precise estimates of nutrient excretion are required.

This is the first study to provide a comprehensive comparison of rates and ratios of N and P excretion across a broad range in taxa. We have developed the first set of multi-species multivariate empirical models for predicting the release of nutrients (N and P) by zooplankton, mussels and benthic macroinvertebrates. These models provide the ability

to simultaneously compare internal regenerative pathways of nutrients by mixed assemblages of aquatic metazoans with other nutrient sources (e.g. internal loading from the sediments and external loading from the catchment) in both marine and freshwater ecosystems. Moreover, the significance of benthic versus pelagic fauna and the relative abundance of different metazoan taxa on nutrient regeneration can now be determined (i.e. how does the relative abundance of zooplankton, mussels, benthic macroinvertebrates and fish influence rates of excretion at the ecosystem level?). These models provide a useful addition to the many empirical models (Nurnberg 1984; Håkanson 1995; Hudson & Taylor 2005; Sereda et al. 2008a) in the literature, and together, begin to establish a comprehensive understanding of nutrient cycling in aquatic ecosystems.

Chapter 4.1: Fish as Sources and Sinks of Phosphorus³

4.1.1. Introduction

The significance of nutrient release by fish for plankton communities is uncertain; many authors have suggested that nutrient release by fish is important (Brabrand et al. 1990; Mather et al. 1995; Persson 1997; Schaus et al. 1997; Vanni 2002) whereas others suggest it is a small contribution (Kitchell et al. 1975; Hudson et al. 1999; Gido 2002; Griffiths 2006). Some of this difference in opinion arises from whether nutrients released by fish are compared to external loading or internal cycling. While nutrient regeneration by fish may be large relative to external loadings in small lakes with limited water input (e.g., Shostell & Bukaveckas 2004), fish are an internal source of nutrients and internal cycling of nutrients (e.g., planktonic regeneration) in lakes is large relative to external loading (Hudson et al. 1999).

Some recent studies have explored the role of fish as benthic-pelagic couplers, transporting and releasing benthic nutrients into the pelagic zone (Schindler & Scheuerell 2002; Vander Zanden & Vadeboncoeur 2002; Vanni 2002). This translocation of nutrients has been considered a source of “new” nutrients for the plankton community (Vander Zanden & Vadeboncoeur 2002). Benthic organisms comprise a significant proportion of the diet of many littoral zone fish species, particularly in small lakes. However, fish undergo ontogenetic (Winemiller 1989), biomass-dependent (Schaus et al. 2002) and seasonal diet shifts due to prey availability (Mehner et al. 1998). Planktivorous fish feeding and releasing nutrients in the pelagic zone only recycle nutrients in the water column and do not provide new nutrients to the plankton community. More importantly, since there is usually no thermal barrier to horizontal movement of nutrients regenerated

³ Contents of this chapter have been published in *Freshwater Biology*. 2008. **52**: 278-289.

by littoral organisms, it is not clear that the involvement of motile organisms such as fish is required for nutrients to reach the plankton; water currents can bring nutrients into the pelagic zone and vice versa. Fish feeding on profundal benthos could also bring new nutrients into the epilimnion, but this is a much less likely migration and the net effect of fish movements between these zones could be to move nutrients out of the euphotic zone.

Nutrient release rates have been estimated through both bioenergetic models (Tarvainen et al. 2002; Bunnell et al. 2005) and direct measurements (Gido 2002; Zimmer et al. 2006). However, parameters of consumption and growth, as well as the nutrient and energy content of both predator and prey, must be known for bioenergetic modelling (Kraft 1992). These parameters are not known for many species, and must often be inferred from other closely related species. Regression models of nutrient release have been developed for single species from direct measurements (Shostell & Bukaveckas 2004; Vanni et al. 2006). These empirical relationships have been applied to fish populations to estimate nutrient release over multiple years. However, these relationships only capture the variability in release rates of a single species, and may not be applicable to other systems. Therefore, the development of an empirical relationship of nutrient release for multiple species would be useful for the rapid estimation of the total nutrients released by all fish in a given waterbody.

Fish may contain a substantial amount of P in their biomass which is unavailable to primary producers. Kitchell et al. (1975) found up to 75% of total phosphorus (TP) in the pelagic zone of Lake Wingra (Wisconsin) was in fish biomass. In addition, they estimated that 30–35% of the annual input of P into Lake Wingra was sequestered into fish biomass. Nakashima and Leggett (1980) estimated that the P content of pelagic fish

in Lake Memphremagog was comparable to that of the seston, and much greater than that of the zooplankton. Kraft (1992) estimated that P sequestered by young-of-the-year yellow perch in Lake Memphremagog (Vermont/Quebec) was similar to P losses from algal sedimentation. Parmenter and Lamarra (1991) estimated that 40% of the total fish P may remain immobilized in bone and scales which, upon death of the fish, may be incorporated into the sediment and lost permanently from the water column. Such studies suggest that fish may be more important as sinks rather than sources of nutrients.

Our study had five objectives. 1. To determine the amount of phosphorus (TP) and nitrogen (ammonium-N) released by the five dominant fish species in Mouse and Ranger Lakes (Ontario) during the summers of 1993 to 1995. 2. To develop empirical relationships of nutrient release of TP and N for multiple species that could be used for the rapid estimation of fish nutrient release in other systems. 3. To compare the release rates of fish to planktonic regeneration rates of P in both lakes. 4. To characterize the stoichiometry of direct P and N release from the fish assemblage. 5. To determine the quantity of nutrients (P and N) bound in fish and plankton, and to compare the P turnover rates of both.

4.1.2. Methods

Study Lakes

This study was conducted at Mouse and Ranger Lakes in south central Ontario. Each lake has a single basin, is oligotrophic, and is found on the Canadian Shield. These lakes undergo stratification during the summer, and share similar morphological and chemical properties (Table 4.1.1). Detailed physical and chemical properties are described in Hudson et al. (2001), McQueen et al. (2001) and Dillon et al. (2001).

Table 4.1.1. Physical and chemical properties of Mouse and Ranger Lakes (from McQueen et al. 2001; Dillon et al. 2001). TP and TKN (Total Kjeldahl Nitrogen) are mean epilimnetic concentrations (1993-95).

	Area (ha)	Mean depth (m)	Max. depth (m)	Mean epilimnetic volume (10^8 l)	TP ($\mu\text{g l}^{-1}$)	TKN ($\mu\text{g l}^{-1}$)
Mouse	9.9	4.9	9	2.87	6.1	255
Ranger	11.2	5.5	13	2.91	6.5	300

Mouse Lake was free of obligate piscivores from 1978 until late 1993, and was characterized by high densities (mean = 2008 ha^{-1}) of small non-piscivorous fish (Demers et al. 2001a). Fish biomass over 1993 to 1995 was $26\text{--}43 \text{ kg ha}^{-1}$. In late 1993 largemouth bass (*Micropterus salmoides* L.) and smallmouth bass (*Micropterus dolomieu* L.) were transferred from Ranger L. to Mouse L. as part of the Dorset Biomanipulation Project (McQueen et al. 2001). Prior to bass removal in late 1993, Ranger L. was characterized by low densities (mean = 30 ha^{-1}) of piscivores (largemouth bass and smallmouth bass) and abundant (mean = 230 ha^{-1}) non-piscivores (Demers et al. 2001a). Fish biomass over 1993 – 1995 was $19\text{--}29 \text{ kg ha}^{-1}$. Following biomanipulation, fish abundance in both lakes was dominated by golden shiners (*Notemigonus crysoleucas* M.), pumpkinseed (*Lepomis gibbosus* L.), yellow perch (*Perca flavescens* M.), largemouth bass, white sucker (*Catostomus commersonii* L.), and smallmouth bass. These six species represented, on average, 85% and 99% of the fish biomass in Mouse L. and Ranger L., respectively.

Measurements

The five most abundant fish species were collected during July and August 1993 (golden shiner, pumpkinseed, yellow perch, and largemouth bass) and 1994 (white sucker). Fish collections in 1993 were completed prior to the transfer of piscivores from Ranger L. to Mouse L. Collections and incubations were completed by Dr. Jeff Hudson (Dept. of Biology, University of Saskatchewan). Fish were collected from both lakes by shoreline seining or angling (largemouth bass only). A broad range in fish size was selected for each species to capture size-related differences in nutrient release. Captured fish were rinsed twice with lake water and transferred with a dip net into incubation containers with 2 to 36 l of lake water depending on fish size. Prior to fish introduction, incubation water was boiled then cooled to ambient temperature to limit ammonia uptake by microorganisms. Two control containers without fish (three for golden shiners and white sucker) were used for each fish species to monitor changes in TP and N concentrations that were not attributable to fish. Incubation containers were kept under low light and noise levels, and were partly immersed in the lake to maintain ambient lake temperatures. Water temperature was monitored throughout the incubations. All incubations began 1–3 h after fish capture. Containers were subsampled (approx. 50 ml, once for TP and once for N analysis) at time 0 and subsequently at approximately 1, 2 and 4 or 5 h unobtrusively through outlet valves. At the end of each incubation the wet mass of each fish was recorded and then fish were sacrificed and stored at -20°C for determination of C, N and P.

TP samples were first oxidized with potassium persulfate and then analyzed using the molybdate blue colorimetric method (Parsons et al. 1984). Ammonium samples were

preserved according to Degobbis (1973) and then analyzed within two weeks for ammonium nitrogen using the phenol-hypochlorite method (Wetzel & Likens 1991). Our measurement of P as TP included all processes (egestion and excretion) that release P into the incubation container. However, our measurements of N only include processes that release NH_4^+ (e.g., excretion) and as a result do not include the release of N in other forms of dissolved or particulate organic N. Changes in the concentration of TP and NH_4^+ in each container were plotted as a function of time and modeled with linear or non-linear regression. The instantaneous release rate ($\mu\text{g h}^{-1}$) of each fish was calculated by taking the derivative at the start of the incubation (i.e., $t = 0$) (Wilhelm et al. 1999).

The contribution that the fish assemblage made to the nutrient supply of each lake was determined as follows. Fish abundance and biomass estimates were calculated as described by Demers et al. (2001a). Briefly, sampling was conducted at 3 to 5 equally spaced intervals from May through September using a series of active (beach seine and electrofishing) and passive (trap netting) sampling. All captured fish were identified to species and up to 500 individuals were measured (fork and total length). Size-stratified subsamples of up to 100 individuals were weighed (nearest 0.1 g), and scales or pectoral spines taken for age determination. Population estimates were calculated each May (1993-1995), and also in August of 1994 and 1995, with Schnabel multiple-census mark recapture experiments (Ricker 1975). Confidence limits for biomass were calculated using the upper and lower limits of density because errors associated with density estimation represent the largest uncertainties in calculating biomass (Demers et al. 2001b). These biomass and abundance estimates were then applied to a bioenergetics model (Hewett & Johnson 1992) with daily estimates for young of the year (YOY),

juvenile, and adult fish abundance, biomass, growth and mortality (Demers et al. 2001b). Estimation of bioenergetic model parameters is described by Demers et al. (2001b).

The rate of nutrient release ($\mu\text{g}\cdot\text{h}^{-1}$) of individual fish of a species ($n \approx 10$ fish/species) was regressed against fish mass. These relationships were then applied to the estimates of fish biomass and abundance ($\pm 95\%$ C.I.) over three years (1993–95) to obtain lake-wide estimates of fish release. Biomass and abundance estimates were obtained from a separate study (Demers et al. 2001b). Release rates of largemouth bass were used to estimate the release rate of smallmouth bass, the sixth most abundant species in both lakes. Release rates for larval fish were not directly measured, but were extrapolated from species specific regressions and were included in whole-lake release rate estimates. Confidence intervals (95%) were calculated for release rates predicted from species-specific regression (Zar 1999). Release rates and associated 95% C.I. were summed for each size class of each species and then for all species combined to provide a total daily release rate ($\pm 95\%$ C.I.) for the entire fish assemblage. Total daily release rates, and associated 95% C.I. were then summed for July and August and a mean daily release rate and C.I. was calculated. We assumed that fish were confined to the oxygenated epilimnetic waters during the summer months in both lakes. Therefore, daily nutrient release by the entire fish assemblage ($\mu\text{g l}^{-1} \text{ d}^{-1}$) was standardized for the mean epilimnetic volume of each lake ($2.87 \times 10^8 \text{ l}$ in Mouse L. and $2.91 \times 10^8 \text{ l}$ in Ranger L.).

Concurrent total epilimnetic planktonic regeneration rates of P were measured using radioisotope techniques for both Mouse and Ranger Lakes according to Hudson and Taylor (1996). Planktonic regeneration rates were measured on three separate dates each

summer (1993–95). Daily nutrient release rates by fish were compared on dates when planktonic regeneration rates were measured.

Elemental composition of each fish was determined using the following procedure. Fish were thawed and the dry mass of each fish was determined. Fish were dried at 80°C, for 12–13 h (independent of fish mass). Fish had been kept frozen for ten years and were already in a dehydrated state; hence only short drying times were required. Fish were first ground with a food processor, and then with a mortar and pestle. TP analysis was conducted with two to three sub-samples (0.0093 to 0.455 g) of homogenized tissue per fish. Sub-samples were acid digested with 3 ml of 70% nitric acid, neutralized with sodium hydroxide (4 mol l⁻¹), and brought up to 50 ml with de-ionized water. Samples were diluted, oxidized with potassium persulfate, and analyzed for TP using the molybdate blue colorimetric method with a spectrophotometer (Parsons et al. 1984). One to two replicates of dried tissue (0.100 to 0.300 g) from each fish were also analyzed on a LECO CNS-2000 carbon-nitrogen analyzer (St-Joseph, Michigan, United States) to determine fish carbon and nitrogen content.

To estimate the quantity of C, N, and P bound in fish biomass we determined fish dry mass for each size class of each species using species specific dry mass to wet mass ratios. Mean percentages of C, N, and P (species specific) were then multiplied by the dry mass of fish. Mass of each element was then summed, for each size class for each species, and then for all species combined. This provided the total mass of nutrients bound in fish biomass each day. Daily totals were then averaged over July and August.

Turnover rates of P and N were then determined. The quantity of P and N bound in fish biomass was divided by the daily quantity of the nutrient released. Turnover rates

were calculated each day, for each size class, for each species. Daily turnover rates accounted for changes in biomass through estimates of growth and mortality. Turnover rates for all species were then averaged over July and August.

Epilimnetic particulate P (i.e., planktonic P) was determined according to Hudson et al. (2001). Epilimnetic total particulate nitrogen was determined on the same water with the identical filter size fractionation procedures that Hudson et al. (2001) used for determining particulate P concentrations. Particulate nitrogen was measured as Kjeldahl nitrogen using the modified atrazine technique outlined by the Ontario Ministry of the Environment (reference E3188 – The determination of solids in liquid matrices by gravimetry, August 19, 2004). With this technique, nitrogen samples were mineralized to ammonia using a hot acid/mercuric oxide digestion. Samples were then neutralized and analyzed using phenate-hypochlorite colorimetry at 630 nm.

Statistical analysis was performed with Statistica Version 6.0 (Tulsa, Oklahoma, United States), and all statistical significance levels were set at $p = 0.05$.

4.1.3. Results

Ambient lake temperatures during the measurements of nutrient regeneration by fish ranged from 22.8 to 25.9°C. Temperature, TP and N concentrations in control containers did not change significantly ($p > 0.05$, model I linear regression) over the course of the incubations. The concentration of TP increased significantly over the course of all fish incubations ($p < 0.05$, $R^2 \geq 0.79$). Instantaneous release rates (at $t = 0$) ranged from 7.69 to 515.6 $\mu\text{g TP h}^{-1}$ (Fig. 4.1.1), and inter-specific differences in P release rates were observed ($F_{1,4} = 2.864$, $p = 0.035$, analysis of covariance (ANCOVA)).

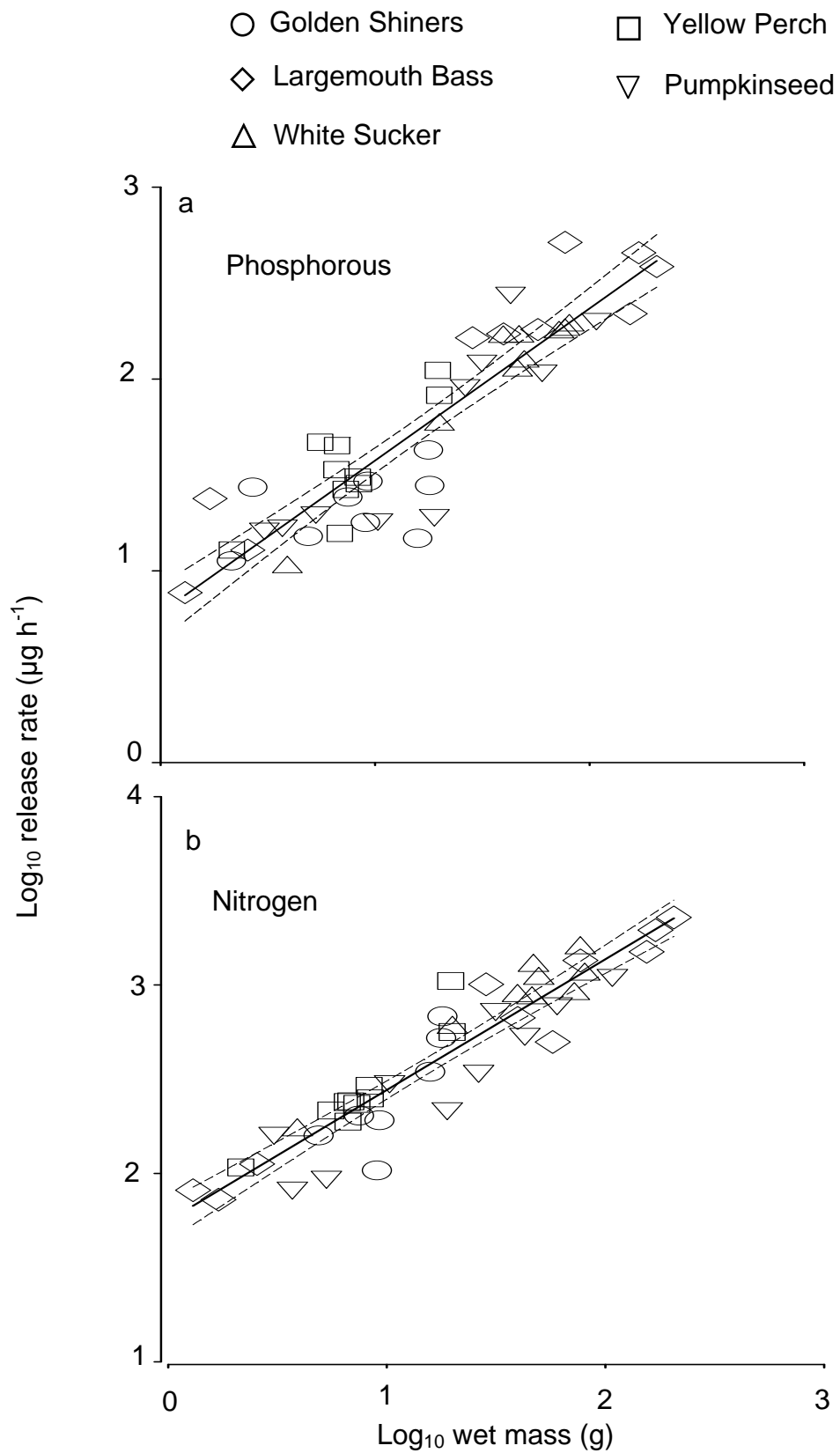


Figure 4.1.1. A) Release of TP by all fish in relation to their wet mass (g), $n = 48$, $R^2 = 0.82$, $p < 0.001$, \log_{10} TP release rate ($\mu\text{g h}^{-1}$) = $0.793(\pm 0.109)$ [\log_{10} wet mass (g)] + $0.7817(\pm 0.145)$. Release rates of P across all species ranged from 7.69 to 515.6 $\mu\text{g h}^{-1}$. B) Release of N in the form of NH_4^+ in relation to wet mass (g) for all fish, $n = 46$, $R^2 = 0.88$, $p < 0.001$, \log_{10} N release rate ($\mu\text{g h}^{-1}$) = $0.6946(\pm 0.079)$ [\log_{10} wet mass (g)] + $1.7481(\pm 0.108)$. Release rates of N across all species ranged from 72.6 to 2282 $\mu\text{g h}^{-1}$. Confidence intervals (95%) for each regression are shown.

Ammonium concentrations (henceforth, N) also increased over time in all fish incubation containers ($p < 0.05$, $R^2 \geq 0.97$), except in two containers where a trend was not evident. The fish in these two containers were very small (< 3 g) and increases in the concentration of N may have been undetectable, or offset by slight losses of N from the containers. The results from these two incubations were not included in subsequent analyses. Release rates of N across all species ranged from 72.6 – 2282 $\mu\text{g h}^{-1}$ (Fig. 4.1.1), but inter-specific differences in N release rates were non-significant ($F_{1,4} = 1.817$, $p = 0.14$, ANCOVA).

Directly measured instantaneous release rates of P and N ($\mu\text{g h}^{-1}$) for all fish were log-transformed and regressed (model I) against the log of fish wet mass (Fig. 4.1.1). Release rates of both nutrients increased with fish mass but at a decreasing rate (i.e., slope of each relationship is less than 1). The total contribution that fish made to the nutrient supply of each lake was calculated over the 3 years of study (Fig. 4.1.2). Total nutrient release for the six main species present in each lake (five species used in incubations, plus smallmouth bass) was 0.053–0.145 $\mu\text{g TP l}^{-1} \text{ d}^{-1}$ (mean = 0.083 ± 0.061 , 95% C.I) and 0.053–0.072 $\mu\text{g TP l}^{-1} \text{ d}^{-1}$ (mean = 0.062 ± 0.020 , 95% C.I) for Mouse L. and Ranger L., respectively. Nutrient release of N (1993 to 1995) was 0.270–0.527 $\mu\text{g l}^{-1} \text{ d}^{-1}$ (mean = 0.41 ± 0.17 , 95% C.I) in Mouse L., and 0.240–0.355 $\mu\text{g l}^{-1} \text{ d}^{-1}$ (mean = 0.31 ± 0.08 , 95% C.I) in Ranger L. Total planktonic release rates of P were 0.38–2.01 $\mu\text{g l}^{-1} \text{ d}^{-1}$ (mean 1.02

± 0.45 , 95% C.I.) (Mouse L.) and $0.64\text{--}1.45 \mu\text{g l}^{-1} \text{d}^{-1}$ (mean 0.85 ± 0.19 , 95% C.I.) (Ranger L.) and were much greater than P regeneration by the fish assemblage (Fig. 4.1.3).

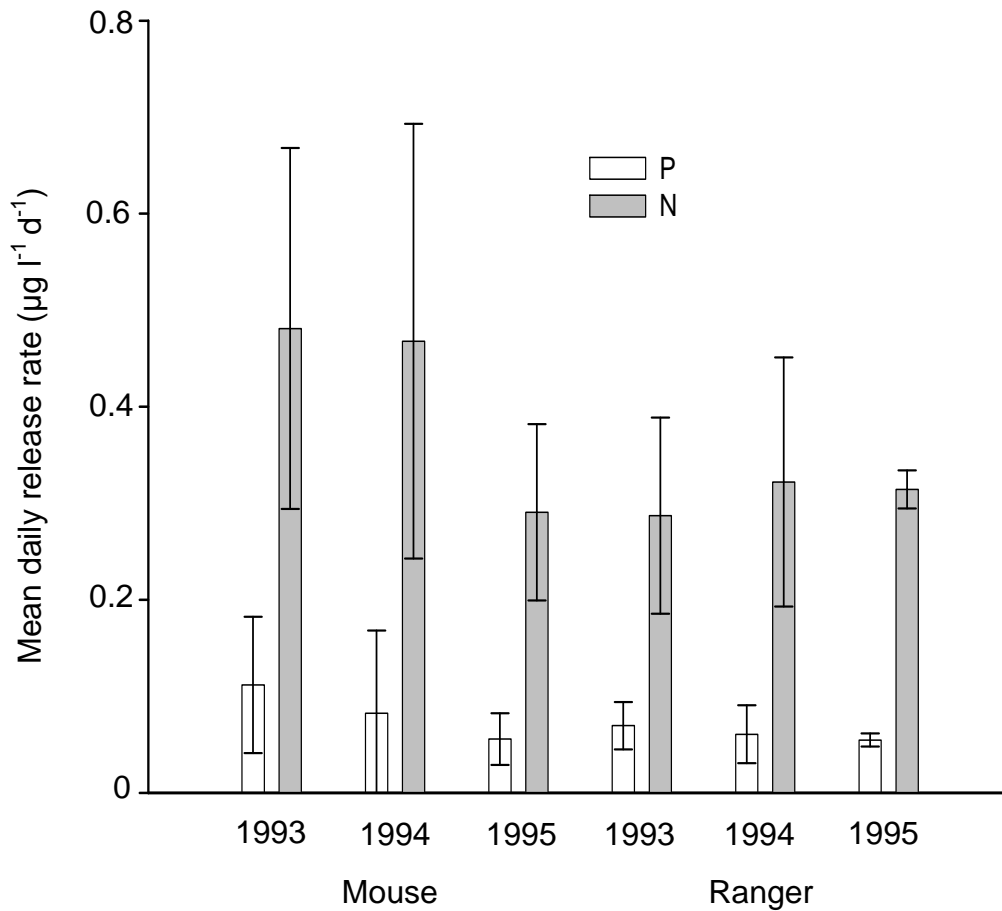


Figure 4.1.2. Mean daily release of P and N ($\mu\text{g l}^{-1} \text{d}^{-1}$) by the fish assemblages in Mouse and Ranger Lakes. Confidence intervals (95%) represent cumulative variance of release rates predicted from species specific regressions of nutrient release, C.I. surrounding fish abundance estimates, and variation between daily release rates (July 1 to August 31) of each year.

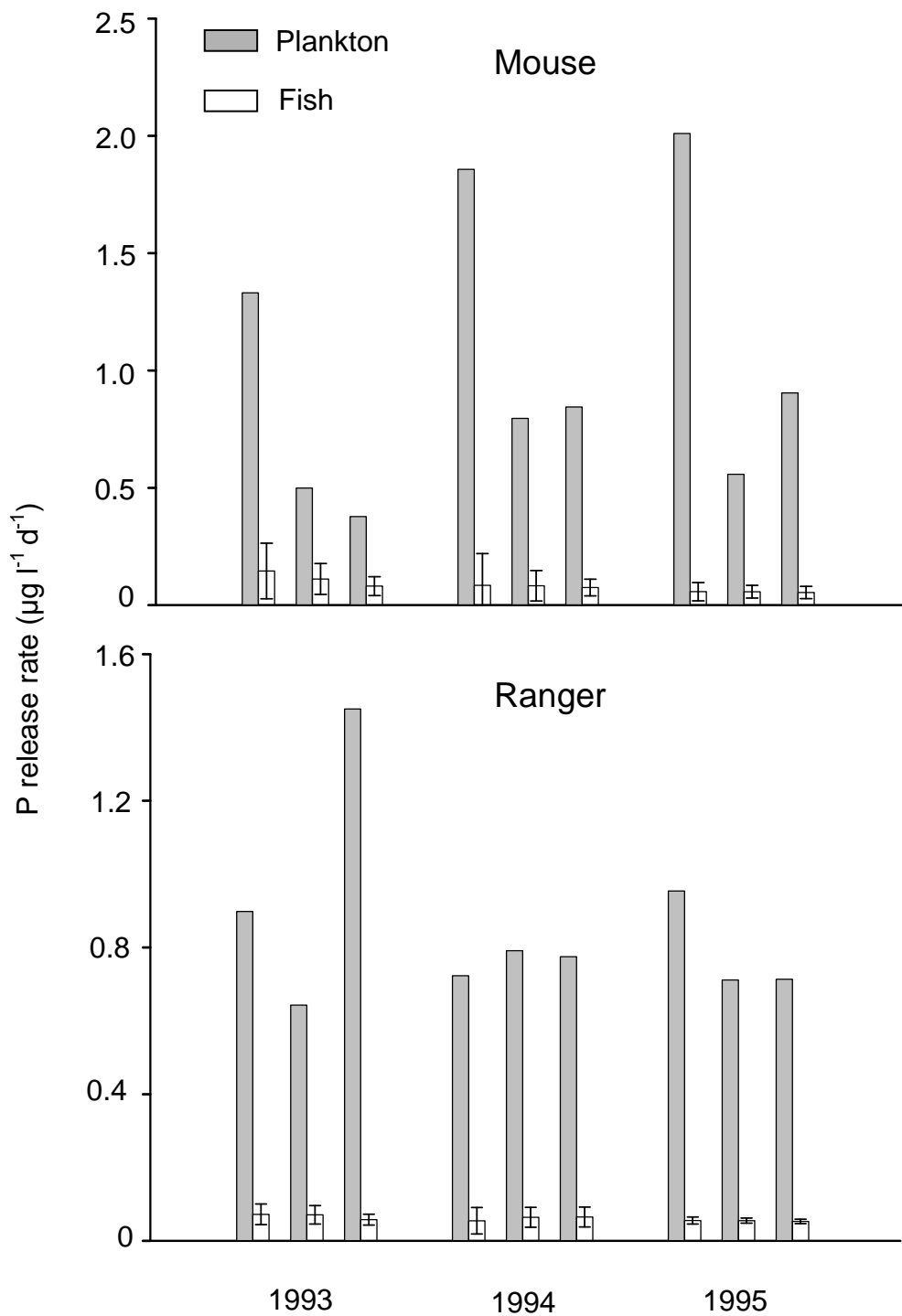


Figure 4.1.3. Comparison of daily release rates of P by the fish assemblage ($\mu\text{g l}^{-1} \text{d}^{-1}$) to regeneration rates of P by the plankton community in Mouse and Ranger Lakes. The 95% C.I. are shown for daily fish release rates. Planktonic regeneration rates are individual measurements and therefore, 95% C.I. are not shown.

The molar ratio of ammonium to TP release (henceforth N:P release ratio) by all fish had a range of 4.3:1 to 54.1:1, with a mean of 18.1:1 (Fig. 4.1.4). White sucker had a significant negative relationship between the N:P ratio of released nutrients and wet mass ($P = 0.02$), but this trend was not observed for other species or when all species were combined. Inter-specific differences in N:P ratios were observed ($F_{1,4} = 2.895$, $p = 0.034$, ANCOVA), but not when two outlying golden shiner values (Fig. 4.1.4) were removed ($F_{1,4} = 1.286$, $P = 0.30$, ANCOVA).

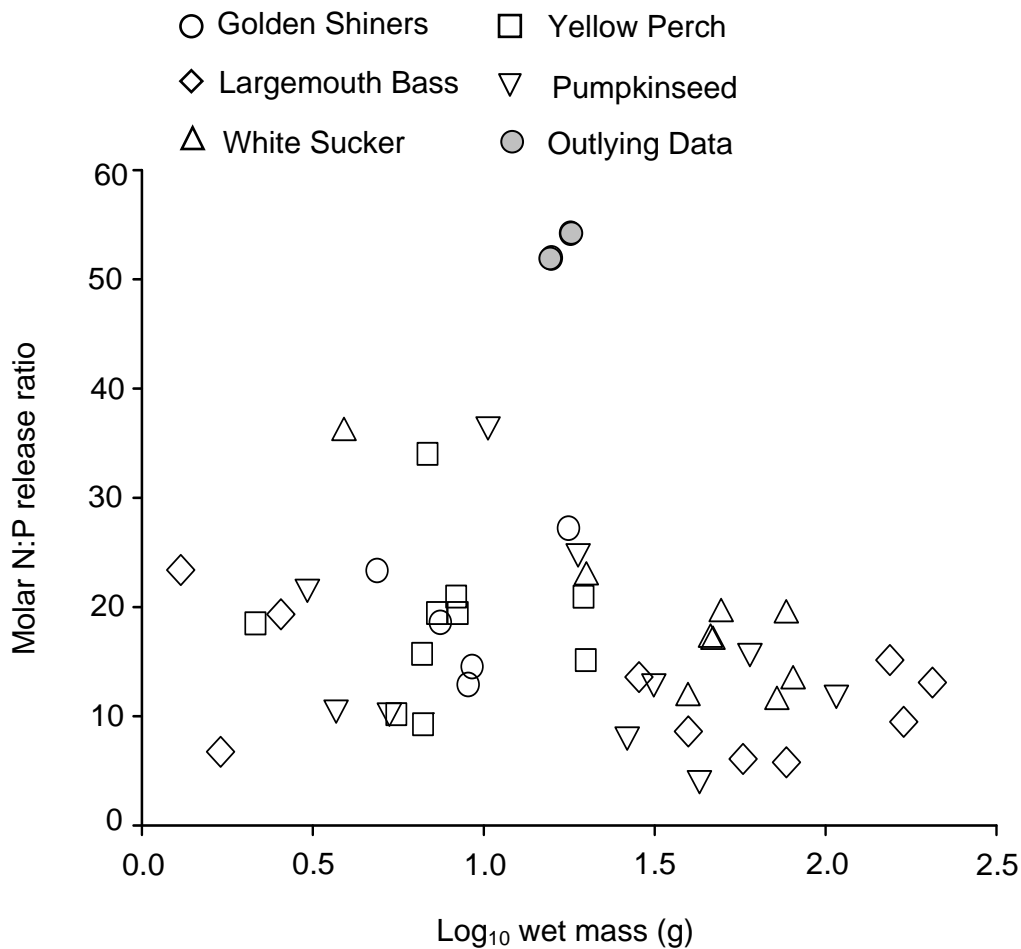


Figure 4.1.4. N:P released by fish (mol:mol) in relation to dry mass (g), $n = 46$, $R^2 = 0.06$, $p = 0.10$, range 4.3:1 to 54.1:1 (mean = 18.1:1). Outlying data points for golden shiners are indicated.

Fish wet mass ranged from 1.3 to 205.5 g, with a mean of 34.6 g. The dry mass of all fish ranged from 16.1% to 38.0% (mean = 22.8%) of initial wet mass. Carbon was 31.9% to 43.9% (mean = 39.3%) of dry mass (Fig. 4.1.5). The carbon content was negatively correlated with dry mass in largemouth bass ($p = 0.0002$), and when data for all fish were combined ($p = 0.008$). Nitrogen accounted for 9.6% to 12.2% (mean = 10.9%) of dry mass. The N content of pumpkinseed was negatively correlated with dry mass ($p = 0.03$). Similar, but non-significant relationships were also found for largemouth bass and when data for all fish were combined ($p = 0.06$ and 0.09 respectively). The phosphorus content of all fish ranged from 2.1% to 5.3% (mean = 4.0%) of dry mass. Phosphorus content was not correlated ($p > 0.05$) with dry mass. The mean molar C:N:P ratio across all species was 27:6:1. Inter-specific differences in body nutrient content were observed (ANCOVA); $F_{1,4} = 6.973, p = 0.0002$, $F_{1,4} = 8.16, p < 0.001$, $F_{1,4} = 10.787, p < 0.001$, for C, N and P, respectively.

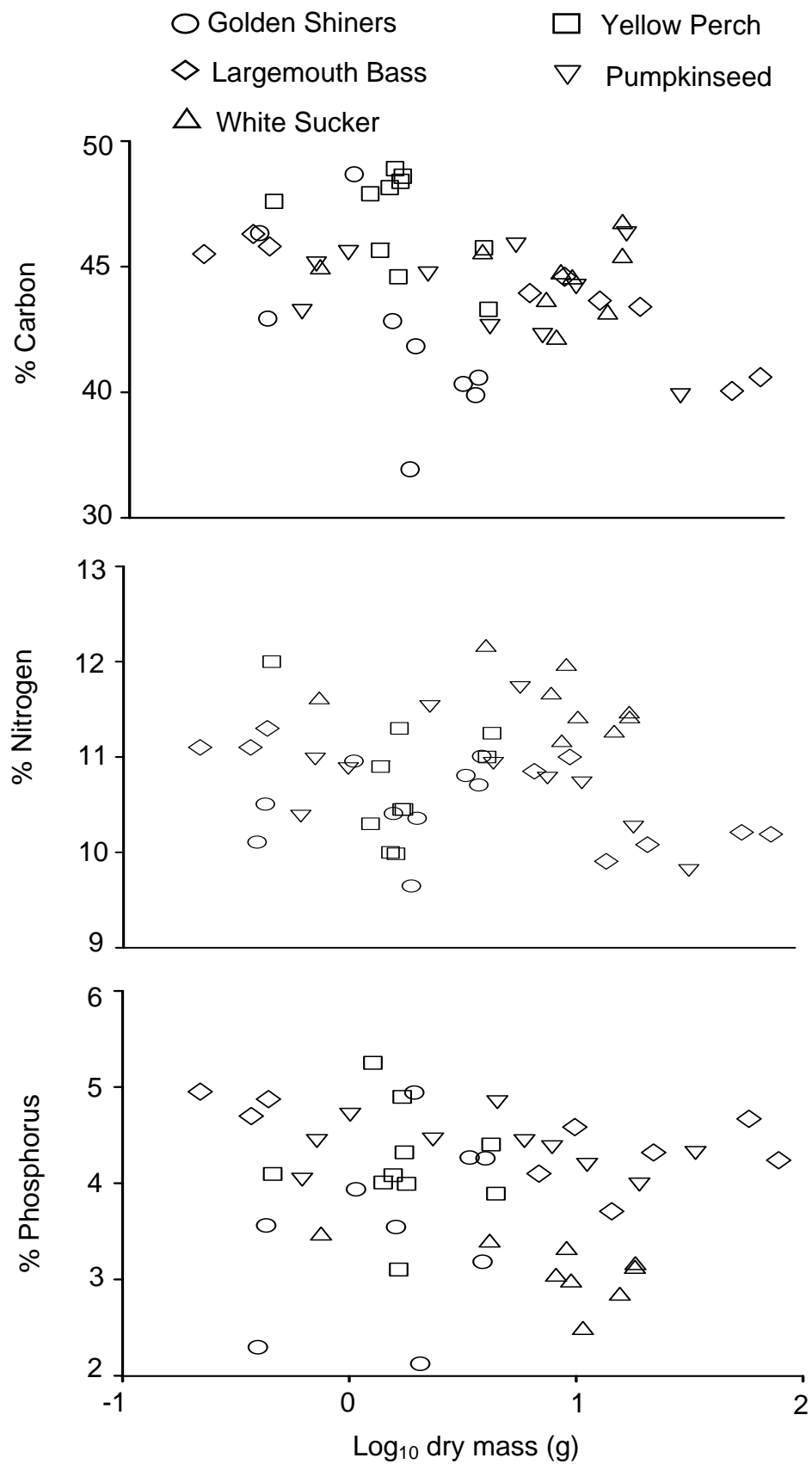


Figure 4.1.5. Carbon, nitrogen and phosphorus content as a percentage of fish dry mass (g), $n = 47$. Each point represents a single fish. Note the log scale of the x-axis. Ranges of elemental composition were C 31.9% to 43.9% (mean = 39.3%), N 9.6% to 12.2% (mean = 10.9%) and P 2.1% to 5.3% (mean = 4.0%).

Approximately 1.58 kg of C, 0.42 kg of N and 0.16 kg of P per hectare were bound in fish biomass in Mouse L. during 1993 to 1995 (Fig. 4.1.6). For Ranger L. the corresponding amounts were 1.54 kg C, 0.42 kg N and 0.14 kg of P per hectare. Turnover rates of phosphorus and nitrogen bound in fish biomass were 96 and 47 days, and 110 and 49 days, for Mouse and Ranger Lakes, respectively. Over the same period, planktonic biomass in the epilimnion contained approximately 1.51 kg N ha⁻¹ and 0.13 kg P ha⁻¹ in Mouse L., and 1.30 kg N ha⁻¹ and 0.12 kg P ha⁻¹ in Ranger L. Turnover rates of phosphorus bound in planktonic biomass were on average 4.8 and 5.3 days for Mouse and Ranger Lakes, respectively.

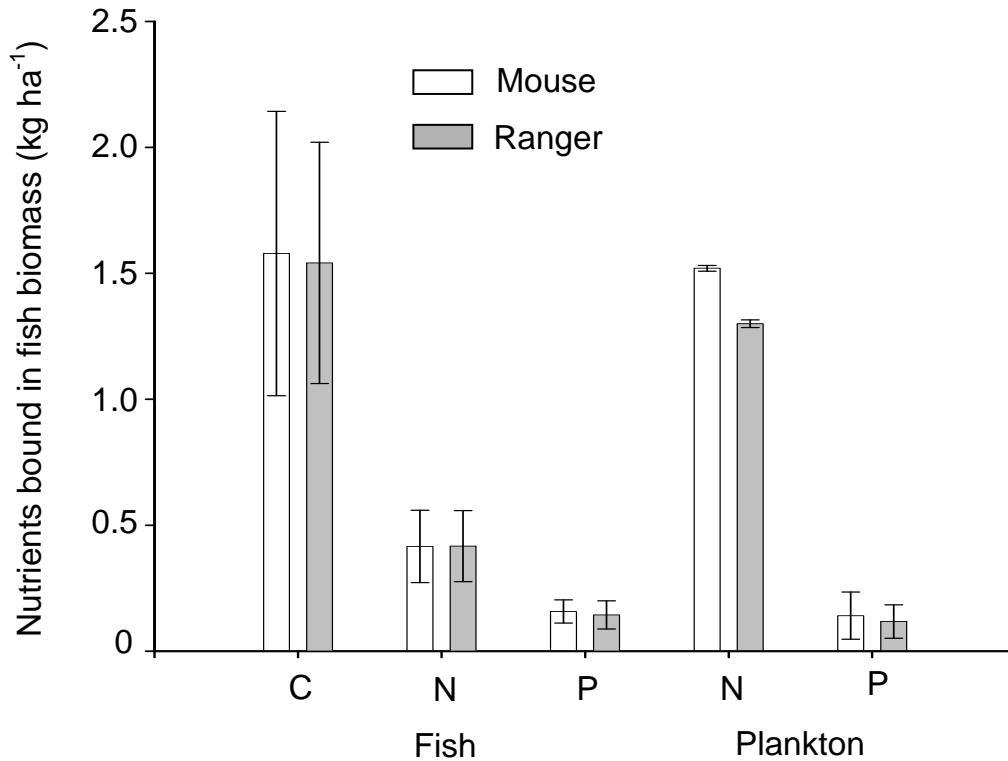


Figure 4.1.6. Mean mass (kg) of C, N and P per hectare bound in fish and plankton in Mouse and Ranger lakes from 1993 to 1995 (95% C.I. are shown). Carbon content of plankton was not measured.

4.1.4. Discussion

Our TP release rates may include some particulate matter that is unavailable to plankton, for example apatite from bone in the case of piscivores. We believe that most of the TP released would have been released as phosphate (PO_4), or available via the action of exo- and ectoenzymes. For example, Brabrand et al. (1990) found that most (85–95%) of the P released by fish was in available form. However, it is possible that our rates of P regeneration may represent slight overestimates.

Unlike our measurements of TP, our measurements of N only measured the release of N as NH_4^+ and may have underestimated total N release. Andre et al. (2003) reported that approximately two-thirds of the total N regenerated by cichlids was in soluble form, of

which 90% was NH_4^+ . The remainder of the N was excreted in other soluble forms (e.g. urea) and egested as faeces. As such, our measurements of N may have only accounted for approximately 60% of the total N released.

Handling stress may potentially increase fish release rates. However, Mather et al. (1995) concluded that handling stress had no significant affect on release rates or ratios. Egestion and excretion rates may be affected by the time elapsed since the fish fed (Tarvainen et al. 2005). Glaholt and Vanni (2005) observed that P excretion rates peaked 2 h after feeding and then returned to a low and constant level. All incubations in this study were started 1 to 3 h after fish were captured. If fish had fed before capture, then our release rates may represent maximum rates because we calculated release rates at $t = 0$; when the incubation started. However, the feeding history of the fish in this study is unknown. Assuming release rates were maximal, applying these rates to the population would overestimate the contribution by fish to the nutrient supply. For example, Schaus et al. (1997) observed daily excretion rates of gizzard shad (*Dorosoma cepedianum* L.) to be 82% of maximum. Alternatively, extended separation from food may have resulted in lower release rates, thereby potentially underestimating the contribution by fish to the nutrient supply. However, we believe that biases in either direction are minor for two reasons. First, our release rates overlap with other directly measured rates from the literature (Table 4.1.2). Secondly, Griffiths (2006) presented a relationship of TP released ($\text{g ha}^{-1} \text{ d}^{-1}$) by fish communities in relation to fish biomass (kg ha^{-1}). This relationship was derived from eight studies, calculating areal nutrient loads by fish communities in 22 lakes. Fish biomass in our lakes was approximately $20\text{--}40 \text{ kg ha}^{-1}$, with areal loading

estimates of 1.2 to 2.5 g ha⁻¹ d⁻¹. These values are similar to those presented by Griffiths (2006). Therefore, our estimates of fish nutrient release appear typical.

Mean daily release rates of P and N did not change substantially across three years of study in Mouse and Ranger lakes (Fig. 4.1.2). The general trend in Mouse L. was a declining mean daily release by the fish community. This is likely a result of decreased fish production following the addition of piscivores in late 1993 (Demers et al. 2001b). From 1993–1995 changes in mean daily P and N release (\pm 95% C.I.) by the fish community in Ranger L. were non-significant. Following the removal of piscivores, fish production increased in Ranger L. (Demers et al. 2001). The quantity of nutrients released is expected to increase with increased fish production. However, substantial increases in fish production did not occur in Ranger L. until after our study was completed (1996–97).

Table 4.1.2. Comparison with other studies of fish release rates of N, P and N:P release ratios (by moles). Nutrients released were NH₄-N (N) and TP unless otherwise stated. All rates, except one (Tarvainen et al. 2002) were determined by direct measurements of release.

Species	Mean fish wet mass (g)	Incubation temperature (°C)	Release rate (µg g ⁻¹ h ⁻¹)		N:P release (mols)	Type of study	Reference
			N	TP			
All species	34.6	23–26	8.68–62.6	0.93–14.0	4.3–54.1	Field	This study
<i>Gymnocephalus cernuus</i> L.	9.84	16–17	5.9	1.4	25.2	Lab	Tarvainen et al. 2005
<i>Rutilus rutilus</i> L.	0+ older	n/a	n/a	15–22.5 2.91–6.67	n/a	Model	Tarvainen et al. 2002
<i>Lepomis macrochirus</i>	1.96	18–22	12.0–15.6 (unfed)	1.0–2.3 (unfed) (SRP)	18–35 (unfed)	Lab	Mather et al. 1995
			34.5–47 (fed)	1.2–5.7 (fed) (SRP)	18–101 (fed)		

			15.2–15.5 (unfed)	1.0 –1.3 (unfed)	33–35 (unfed)		
<i>Dorosoma cepedianum</i>	18.7	18–22	5.9–101.3 (fed)	2.0 –13.7 (fed)	3–35 (fed)	Lab	Mather et al. 1995

To test the usefulness of our two nutrient release relationships (Fig. 4.1.1) we applied our relationships to fish species used in other nutrient release studies that measured nutrient release directly (Table 4.1.3). Our predicted rates were comparable to those reported in these studies. However, extrapolation beyond the limits of fish mass in the regression resulted in large 95% C.I relative to the predicted release rate. Therefore, expanding these relationships to include a broader range in fish mass would improve their predictive capabilities. Other multi-species nutrient release models have been developed by Schindler and Eby (1997). However, these models were derived from bioenergetic modelling and require knowledge of fish diet and prey nutrient content. Our relationships are derived from direct measurements of planktivorous, zoobenthivorous, and piscivorous fish (Demers et al. 2001b) and capture the variability in nutrient release derived from variations in diet for a broad range in fish size. Therefore, our empirical relationships of nutrient release may be useful for the rapid determination of nutrient release by fish in future studies.

Nutrient release by fish represents approximately 1%– 6% (mean 8%) of the planktonic regeneration rate in Mouse L. and 3%–15% (mean 7%) of planktonic regeneration in Ranger L (Fig. 4.3). If we had included the P regeneration rates of the metalimnetic plankton ($1.11 \mu\text{g P l}^{-1}\text{d}^{-1}$ in Mouse L. and $0.97 \mu\text{g P l}^{-1}\text{d}^{-1}$ in Ranger L.: Hudson & Taylor 1996), the relative contribution by fish would be even less. These observations are consistent with the results of other studies. For example, Griffiths (2006) reported fish to regenerate an average of 6% of the P regenerated by plankton (comparison of 13 lakes from 10 studies using the empirical model by Hudson et al. (1999)). Nakashima and Leggett (1980) found that the P supplied by yellow perch in

Lake Memphremagog only represented 0.06 to 0.17% of the seston daily summer requirements. Gido (2002) estimated that benthic fish of Lake Texoma released a comparatively small amount of P ($0.12 \mu\text{g P l}^{-1} \text{d}^{-1}$) relative to plankton (2.58 to $14.36 \mu\text{g P l}^{-1} \text{d}^{-1}$). In summary, fish are minor regenerators of P relative to plankton in the pelagic zone of Mouse and Ranger Lakes, and this appears to be generally true of lakes.

Across all species, nitrogen release rate declined relative to the phosphorus release rate with increasing fish wet mass (Fig. 4.1.4). The ratio of N released to total phosphorus released (N:P release ratio) was variable, 4.3:1 to 54.1:1 by moles.

Table 4.1.3. Comparison of predicted TP and N (N in NH_4^+) release rates with release rates from other studies. Release rates presented as a range represent observed rates for all fish in the study. Predicted rates were calculated with our empirical fish release relationships (Fig. 1), and the fish wet mass reported in each study. TP, SRP, $\text{NH}_4\text{-N}$ and total ammonia nitrogen (TAN) were the release products measured from each study. Predicted release rates overlap with rates reported from other studies (* mean).

Species	Fish wet mass (g)	Reported P release ($\mu\text{g g}^{-1} \text{h}^{-1}$)	Predicted TP Release ($\mu\text{g g}^{-1} \text{h}^{-1}$)	Reported N release ($\mu\text{g g}^{-1} \text{h}^{-1}$)	Predicted $\text{NH}_4\text{-N}$ release ($\mu\text{g g}^{-1} \text{h}^{-1}$)	Study
<i>Gymnocephalus cernuus</i>	9.84 *	1.4 (TP) *	3.77 ± 2.74	15.9 * ($\text{NH}_4\text{-N}$) 24 * (TAN)	27.9 ± 2.02	Tarvainen et al. 2005
<i>Lepomis macrochirus</i>	1.96 *	1.2–5.7 (SRP)	5.26 ± 2.81	34.5–47.0 ($\text{NH}_4\text{-N}$)	45.6 ± 2.06	Mather et al. 1995
<i>Dorosoma cepedianum</i>	2.2	2.0–13.7 (SRP)	5.14 ± 2.80	5.9–101.3 ($\text{NH}_4\text{-N}$)	44.0 ± 2.02	Mather et al. 1995
	18.7		3.30 ± 2.74		22.9 ± 2.01	
	23.27		3.15 ± 2.74		21.4 ± 2.01	
	48		2.71 ± 2.76		17.2 ± 2.02	
<i>Stizostedium vitreum</i> M.	3.3	n/a	4.72 ± 2.75	30.1 (20°C) (TAN)	38.9 ± 2.04	Forsberg & Summerfelt 1992
	5.6		4.23 ± 2.74	45.2 (25°C)	33.1 ± 2.03	
<i>Cyprinus carpio</i> L.	390	1.2 (TP)	1.76 ± 2.77	n/a	9.05 ± 2.03	Lamarra 1975

	780	1.0	1.52 ± 2.79		7.33 ± 2.04	
<i>Sander lucioperca</i> L.	11.7*	n/a	3.64 ± 2.74	21.2 * (TAN)	26.4 ± 2.02	Zakés et al. 2001

Our results overlapped with the results of other studies, which is not surprising given the broad range we found (Table 4.1.2). When all fish were combined, the mean N:P ratio was 18.1:1 (± 3.14 , 95% C.I.). Some previous studies (Schaus et al. 1997; Levine & Schindler 1999; Attayde & Hansson 2001) have suggested that the low N:P ratio of nutrient regeneration by fish may favour algal communities dominated by Cyanobacteria. However, since the quantity of nutrient released is small relative to other sources, it probably has only a minor influence on plankton. In addition, our N:P ratios, as well as those of other studies (Table 4.1.2) overlap with the Redfield ratio and therefore would be unlikely to favour Cyanobacteria over other algae.

Fish biomass contains approximately $0.16 \text{ kg P ha}^{-1}$ in Mouse L. and $0.14 \text{ kg P ha}^{-1}$ in Ranger L. This represents approximately 55% and 54% of the epilimnetic P (planktonic P and P bound in fish biomass) in Mouse and Ranger Lakes, respectively. Average turnover time for P bound in fish biomass would be 103 days. Fish biomass contained approximately 0.42 kg ha^{-1} of N in both Mouse and Ranger Lakes (Fig. 4.1.6). This represents approximately 22% and 24% of the epilimnetic N (planktonic N and N bound in fish biomass) in Mouse L. and Ranger L., respectively. Average turnover time for N bound in fish biomass would be 48 days. The plankton community accounted for approximately 45% of the epilimnetic P (planktonic P and P bound in fish biomass) or $0.13 \text{ kg P ha}^{-1}$ in Mouse L., and 46% of the epilimnetic P or $0.12 \text{ kg P ha}^{-1}$ in Ranger L. Planktonic regeneration rates of $1.02 \mu\text{g l}^{-1} \text{ d}^{-1}$ (Mouse L.) and $0.85 \mu\text{g l}^{-1} \text{ d}^{-1}$ (Ranger L.), would turn over the planktonic P pool every 4.8 and 5.3 days, respectively. Other studies have reported similar planktonic P turnover times of 4 to 8 days in a variety of other pelagic environments (Dodds et al. 1991; Taylor & Lean 1991; Thingstad et al. 1993;

Van Den Broeck et al. 2004; Flaten et al. 2005). The slow turnover time of fish compared to plankton confirms that fish are important sinks for nutrients (Bartell & Kitchell 1978; Griffiths 2006).

Past studies have suggested that fish may be important suppliers of nutrients to the pelagic zone of lakes (Kraft 1993; Schaus et al. 1997; Vanni et al. 2006). The effect of released nutrients on pelagic primary production will be influenced by the location of the fish in the lake at the time of release (Kraft 1993). Fish may move nutrients from the benthic or littoral zones to the pelagic zone by feeding in the benthic or littoral zone and then swimming to and releasing nutrients in the pelagic zone. Conversely, fish could forage in the plankton at night and retreat to deeper water or nearshore structure during the day. The location of fish in Mouse and Ranger Lakes was determined by beach seining, trap netting, purse seining, electrofishing, angling, Miller trawling, telemetry, and snorkelling surveys (Demers et al. 2001a; unpublished data). YOY golden shiner, pumpkinseed and yellow perch were observed to feed and remain in the pelagic zone. Therefore, these YOY recycled pelagic nutrients, and would not be expected to import nutrients to the pelagic. Meanwhile, older age-classes of fish were observed to feed and remain in the littoral zone. Therefore, evidence of fish feeding in the benthic and littoral zone and then movement to the pelagic zone was not evident in Mouse and Ranger Lakes. Either way, one might expect the horizontal relocation of nutrients by water movements alone to be relatively large compared to the release of nutrients by fish.

In conclusion, we found fish to be minor contributors to the nutrient supply of both lakes, relative to the plankton community. On the other hand, fish biomass contained over 50% of the particulate P and approximately 25% of the particulate N in the epilimnion of

Mouse and Ranger Lakes. While fish are rich in P, the nutrient content of fish and fish excretion does not deviate greatly from Redfield ratios and they are unlikely to cause stoichiometric effects. Other than as sinks, the greatest effect of fish on pelagic food webs is more likely to be through size-selective predation and resulting effects on nutrient cycles.

Chapter 4.2: The Significance of Fish Carcasses in Phosphorus Cycling⁴

The contribution of fish and their relative importance in the nutrient dynamics of lakes (sink vs. source) continues to be a topic of debate (Mehner et al. 2007; Wurtsbaugh 2007; Sereda et al. 2008b). Much of this debate is a result of the context under which fish are compared (Hudson et al. 1999; Wilhelm et al. 1999). Fish represent an internal regenerative pathway of nutrients, and in turn should be compared with other internal pathways (i.e., internal loading from the sediments and planktonic regeneration). However, studies continue to conclude that the regeneration or recycling of nutrients from fish (through excretion or decomposition) are a significant source of phosphorus (P) by comparing fish with a single and often trivial supply route such as allochthonous inputs (Kitchell et al. 1975; Schaus et al. 1997; Schindler et al. 2001).

A recent study by Chidami and Amoyt (2008) offered novel insight into the role of fish in the phosphorus cycle of lakes. The authors sought to test several key hypotheses concerning the fate of fish carcasses in limnetic systems. Most notably, Chidami and Amoyt (2008) ask whether fish carcasses are buried upon deposition, and if not, what is the half-life of the carcass undergoing vertebrate scavenging or bacterial decomposition. The authors concluded that fish were not buried upon deposition and thus were susceptible to both vertebrate scavenging (littoral zone) and bacterial degradation

⁴ Contents of this chapter have been published in *Limnology and Oceanography*. 2010. **55**: 463-465.

(hypolimnion). Chidami and Amyot (2008) point out that water temperature may be used to estimate rates of fish carcass decomposition. The empirical relationships they provide add to a growing literature of empirical models that provide the ability to rapidly calculate rates of internal nutrient recycling (Nürnberg 1984; Hudson & Taylor 2005; Sereda et al. 2008a). They calculated that carcass biomass of a single species (white sucker, *Catostomus commersonii*) could account for 68% of the aqueous P pool, and natural mortality of this species was equivalent to 13.5% of particulate P sedimentation in Lake Croche. The authors concluded that fish carcasses may represent a significant flux of P. This latter point is where we disagree with authors Chidami and Amyot.

Chidami and Amyot (2008) have calculated that a natural mortality (502 kg of biomass) of a single species (white sucker) may account for an annual flux of 2.5 kg P in the East basin of Lake Croche. However, we suspect that these values are anomalous and do not reflect the contribution of natural fish mortalities to nutrient fluxes in oligo-mesotrophic lakes. Chidami and Amyot (2008) have based these calculations on estimates of white sucker biomass and mortality which have been reported in a study by Verdon and Magnin (1977). Verdon and Magnin (1977) estimated a standing stock of white sucker biomass of 2900 kg km⁻² (681 kg total lake wide biomass), with ~84% of the white sucker population (~572 kg) residing in the East basin of Lake Croche. Therefore, the standing stock of white suckers in the East basin (0.06 km²) is 9500 kg km⁻², a biomass considerably greater than what has been reported for other oligo-mesotrophic Canadian shield lakes (mean for the entire fish assemblage = 3000±700 SE kg km⁻², $n = 26$; Fraser 1981; Kelso 1985; Kelso & Johnson 1991). Furthermore, Chidami and Amyot (2008) estimate that 88% (502 kg) (74% of the lake wide standing stock) of

the white sucker biomass in the East basin is lost to annually to natural mortality. If we account for annual production of white suckers, 163.8 kg (~138 kg for the East basin) (Verdon & Magnin 1977) an annual mortality of 502 kg would still represent 71% of the white sucker biomass. These estimates are greater than estimates of annual fish mortality reported by other studies; a range of 10% to 67% (Lorenzen 1996; Schneider 1998; Mills et al. 2002) with a mean of 25% (Reznick et al. 2002). Consequently the large flux of P from white sucker carcasses in the East basin of Lake Croche is a result of an exceptionally great density of fish biomass and abnormally high annual mortality rate. Based on mean standing stock estimates for oligo- mesotrophic Canadian shield lakes (3000 kg km^{-2}), typical mean total fish biomass (all species combined) would be approximately 180 kg for the East Basin (or ~570 kg for the entire lake, 0.19 km^{-2}). Assuming a range in annual mortality rate of 10% to 67% (Lorenzen 1996; Schneider 1998; Mills et al. 2002), we estimate carcass biomass from annual fish mortality to be approximately 18–121 kg, or 4–24% of the author's estimate for only white suckers. In turn, fish carcasses may only represent a P flux of 0.09–0.61 kg instead of 2.5 kg.

However, regardless of the estimate of fish biomass or the rate of mortality applied, we contest the notion that fish carcasses (in the absence of mass mortality events) represent a significant flux of nutrients in lakes. For comparison, we have applied the equations of Sereda et al. (2008a) to conservatively calculate the mass of P regenerated through excretion by an equal mass (502 kg) of fish. Excretion rates were calculated for only the summer months (June through September) when water temperatures are highest and the contribution of fish excretion to the nutrient supply is expected to be most significant. Further, we calculated rates of planktonic P regeneration for epilimnetic

waters in the East Basin during the summer months (June through September) by applying the equation of Hudson and Taylor (2005) to a mean total phosphorus (TP) of $10 \mu\text{g l}^{-1}$ (Chidami & Amyot 2008). Epilimnetic volume was assumed to account for 67% of lake volume (based on mean lake depth = 5.1 m and a mean summer mixing depth of 3.4 m (Carignan et al. 2000). Total lake volume was $877,000 \text{ m}^3$ (Chidami & Amyot 2008) and the East Basin accounted for approximately 30% of the total lake area. Approximately $4.0 [\pm 0.49, 95\% \text{ confidence interval (CI)}]$ kg and $25 (\pm 0.04, 95\% \text{ CI})$ kg P may be regenerated by fish and plankton, respectively. Thus, the P supplied (2.5 kg) by the annual mortality of white suckers is approximately 63% and 10% of the P regenerated by fish excretion and plankton, respectively. However, based on our estimates of fish biomass (180 kg), the P supplied from fish carcasses (18–121 kg) only represents 7–48% and 0.4–2% of the P regenerated by fish excretion and planktonic regeneration, respectively.

Chidami and Amyot (2008) estimated that the downward flux of P (2.5 kg) in fish carcasses may be equivalent to 13.5% of particulate P sedimentation. However, based on our biomass estimates, the downward flux of P (0.09–0.61 kg) in fish biomass may only equal 0.5–3% of particulate P sedimentation in oligo- mesotrophic lakes. Furthermore, our estimates of P excretion by fish are conservative and do not account for nutrients egested as faeces. Approximately 50% of all nutrients released by fish may be egested as faeces which may be deposited in the sediments (Porter et al. 1987; André et al. 2003). Therefore, by comparison the downward flux of egested nutrients (i.e., faeces) by fish may be 47–93% greater than rates of nutrient deposition through the loss of fish carcasses.

Furthermore, Chidami and Amyot (2008) did not monitor all of the decomposition of the fish (i.e., bones and scales) when calculating decomposition half-life. Approximately 50% of fish P may be sequestered in recalcitrant bone and scale (Kitchell et al. 1975; Parmenter & Lamarra 1991). Therefore, the half-life calculated by the authors may represent the decomposition and presumably release of only 50% of the all of the P bound in fish carcasses. Moreover, up to 50% of the fish carcasses deposited in the littoral zone may be scavenged and removed from the system by terrestrial vertebrates (Chidami & Amyot 2008). Therefore, of the 2.5 kg of TP in fish carcasses (assuming 100% deposition in the littoral zone), 1.25 kg TP may be removed from the system by terrestrial vertebrates (Chidami & Amyot 2008, fig. 6). Of the remaining 1.25 kg TP, only half of the TP (0.625 kg) not in bone and scales may be susceptible to rapid degradation. Thus, the annual mortality of white suckers may contribute only 16% and 2.5% (or 2–12% and 0.09–0.61% based on our fish biomass estimates) of the P supplied through fish excretion and planktonic regeneration, respectively. These inputs may be even less if there are further losses of P to direct sediment binding while the carcasses decompose on the sediments.

Finally, in the presence of scavenging fish species TP sequestered in fish carcasses may be directly returned to the top of the food chain through a ‘vertebrate loop’ (Chidami & Amyot 2008, fig. 6). Despite rapid decomposition rates, the recycling of P within a vertebrate loop re-enforces the role of fish as a nutrient sink rather than a source for primary producers in lakes. Considering fish carcasses are rarely observed in shallow lakes the transfer of fish derived nutrients into terrestrial and aquatic vertebrates may be a dominant pathway (Schneider 1998).

In summary, we believe that Chidami and Amyot (2008) have overstated the importance of fish carcasses to the P flux of lakes. The large flux of P (2.5 kg) reported by Chidami and Amyot (2008) results from an exceptionally great density of fish biomass (9500 kg km⁻²) and an abnormally high annual mortality rate (88%). Consequently, the contribution of fish carcasses to the P flux in Lake Croche is not indicative of most oligo-mesotrophic lakes. The significance of fish carcasses to the nutrient flux in lakes is minor when compared to other internal pathways (e.g., excretion and egestion by fish, and planktonic regeneration). However, fish may function as a significant nutrient sink sequestering nutrients which may be returned to the top of the food chain through a vertebrate loop or lost from the system through scavenging by terrestrial vertebrates (Chidami & Amyot 2008). Further research on the fate of fish bones and their significance on the long term sequestering of P in lakes is required. Despite our focus on P fluxes, we assert that similar conclusions would be attained for other nutrients and possibly contaminants.

Nonetheless, we commend Chidami and Amyot (2008) for applying a novel approach to determining the fate of fish carcasses in lakes. The authors have demonstrated that fish carcasses may not be buried upon deposition and are susceptible to bacterial and vertebrate scavenging. Furthermore, the authors demonstrate that water temperature may be a promising predictor of fish decomposition rate. Their empirical models may be applied to aquatic ecosystems where estimates of fish mortality are available. A comprehensive understanding of internal P recycling is developing and the relevance of any single regenerative pathway to the overall nutrient budget of a lake may soon be determined.

CHAPTER 5: Effects of Ultraviolet Radiation on Phosphorus Kinetics⁵

5.1. Abiotic Effects

5.1.1. Introduction

Dissolved organic phosphorus (DOP) is found at concentrations in the epilimnia of lakes that are orders of magnitude greater than PO_4^{3-} (Hudson & Taylor 2005). The DOP pool may be a significant source of phosphorus (P) when the dissolved inorganic P (DIP) pool becomes depleted (Thingstad et al. 1993; Monaghan & Ruttenberg 1999; Cavender-Bares et al. 2001).

The bioavailability of dissolved organic matter (DOM) and associated nutrients (i.e., nitrogen (N) and P) may increase following ultraviolet radiation (UVR) exposure (Kieber et al. 1990; Mopper et al. 1991; Wetzel et al. 1995; Bushaw et al. 1996; Kieber et al. 1999; Vahatalo et al. 2003). For example, the release of orthophosphate from dissolved organic matter following exposure to ultraviolet radiation (UVR) has been reported for a number of lakes (Francko & Heath 1979; Francko & Heath 1982; Cotner & Heath 1990; Zhou 1996). These studies used measurements of soluble reactive phosphorus (SRP) to determine increases in PO_4^{3-} concentration; SRP grossly overestimates measurement of PO_4^{3-} concentration (Hudson et al. 2000) and more advanced approaches are warranted to quantify this potentially important P pathway. For example, slight changes to the concentration of the PO_4^{3-} pool (i.e. resulting from the photodecomposition of DOP to PO_4^{3-}) can be detected with uptake assays of radiophosphate (Lean & Nalewajko 1979; Lean 1984). These provide an uptake constant (k) which is the reciprocal of the turnover time of the phosphate pool.

⁵ Contents of this chapter have been published in *Aquatic Sciences*. 2009. **71**: 127-134.

However, PO_4^{3-} may not be released in detectable concentrations from DOM following UVR exposure. For example, Heath (1986) was unable to detect the release of P from DOM on studies of four lakes. The presence of Fe^{3+} and humic substances in the epilimnion may be necessary precursors for the production of PO_4^{3-} from DOP (Francko 1986; Cotner & Heath 1990). For example, both Cotner and Heath (1990) and Vahatalo et al. (2003) have demonstrated that in lakes with low concentrations of Fe^{3+} and DOM, detectable concentrations of PO_4^{3-} may not be released through photodecomposition processes. However, Zhou (1996) has suggested the presence of oxidizing agents such as photochemically produced hydroxyl radicals may be important in the release of photosensitive P.

Hydroxyl radical production may occur through the photolysis of nitrate (NO_3^-) (Zellner et al. 1990; Mack & Bolton 1999) and photo-Fenton reactions in lakes with high concentrations of DOM and Fe (Zepp et al. 1992; White et al. 2003). However, the rate of radical production through either pathway is pH dependent, with radical yields decreasing with increasing pH (Zellner et al. 1990; Zepp et al. 1992).

Consequently, both the presence and the detection of photolabile DOP compounds in the surface water of lakes may be highly dependent on lake chemistry (i.e., concentrations of DOM, Fe, NO_3^- , TP, and pH). In this study, we have used changes in the turnover time of the PO_4^{3-} pool to determine if detectable quantities of PO_4^{3-} were liberated from PAR+UVR exposed lake filtrate ($< 0.2 \mu\text{m}$) collected from the epilimnion of three thermally stratified lakes.

5.1.2. Methods

The effects of UVR exposure on P cycling were examined in three thermally stratified Canadian Shield lakes (Muskoka, Brandy, and Plastic) located in South Central Ontario. These lakes were selected for their chemical gradients in DOC, pH, TP, Fe, and NO_3^- (Table 5.1.1). Lakes were sampled 1-2 times during July, 2007. Further information on lake characteristics may be found in Dillon and LaZerte (1992), Welsh et al. (1996), and Vander Zanden and Rasmussen (1999).

Epilimnetic lake water (~20 l) was collected 1–2 m below the surface with a Van Dorn bottle from central locations at Brandy and Plastic Lakes, and in South Bay of Lake Muskoka. Water was gently decanted into a collapsible polyethylene bag. All experimental containers were washed (0.1% Contrad-70), leached (0.1M HCl), and rinsed with lake water (polyethylene bag), or distilled water (incubation containers). Epilimnetic water temperature was recorded, and the vertical attenuation of photosynthetically active radiation (PAR) and UVR (at 305, 320, 340 nm) in the water column was measured with a Biospherical BIC compact 4-channel radiometer (Biospherical Instruments, San Diego CA). Vertical attenuation coefficients were determined from the slope $\ln(\text{wavelength (nm) or PAR})$ vs. depth (Table 5.1.2). Water samples were transported to the laboratory in a cooler.

Table 5.1.1. The physical and chemical properties for Muskoka, Brandy and Plastic Lakes (Welsh et al. 1996; Vander Zanden & Rasmussen 1999). Total iron (Fe), and nitrate concentrations represent ten year means (1988–2007) obtained from the Ontario Ministry of Environment’s Dorset Environmental Science Center. Total phosphorus (TP), total dissolved phosphorus (TDP) and dissolved organic carbon (DOC) concentrations are expressed as means plus standard errors (S.E.).

Lake	Latitude (°N)	Longitude (°W)	Area (ha)	Mean depth (m)	pH	TP ($\mu\text{g l}^{-1}$)	TDP ($\mu\text{g l}^{-1}$)	DOC (mg l^{-1})	Fe ($\mu\text{g l}^{-1}$)	Nitrate ($\mu\text{g l}^{-1}$)
Muskoka	45°03'	79°29'	12215	8.7	6.7	5.9 (0.21)	3.8 (0.10)	4.5 (0.06)	31.0	171.6
Brandy	45°06'	79°31'	108	3.5	7.02	24.9 (0.30)	14.2 (0.32)	11.2 (0.04)	328.6	26.25
Plastic	45°11'	78°50'	31	7.9	5.97	4.8 (0.54)	2.87 (0.13)	2.5 (0.09)	35.7	10.30

Table 5.1.2. PAR and UVR were measured with a Biospherical BIC compact 4-channel radiometer (Biospherical Instruments) at three wave lengths [305, 320, and 340 nm, and for the entire photosynthetically active radiation spectrum (PAR)]. Vertical attenuation coefficients (k) were determined from the slope \ln (wavelength (nm) or PAR) as a function of depth. Attenuation coefficients are based on one measurement for Plastic L., and a mean of multiple measurements for L. Muskoka ($n = 3$) and Brandy L. ($n = 2$).

Lake	K_{PAR} (m^{-1})	K_{340} (m^{-1})	K_{320} (m^{-1})	K_{305} (m^{-1})
Muskoka	0.917	7.95	10.46	12.21
Brandy	2.34	22.16	27.79	31.43
Plastic	0.363	1.57	2.18	2.87

Gentle syringe filtration was used to collect lake filtrate by passing whole lake water through a glass fiber filter (GF/F, Whatman, 47mm) and then through a 0.2 μm polycarbonate filter (Poretics, 47mm). Filtrate (100 ml) was placed into 180ml translucent polypropylene containers (Starfrit®). Three treatments (3 replicates per treatment) were established (Fig. 5.1.1); filtrate exposed to indirect sunlight (shade), filtrate exposed to photosynthetically active radiation only (PAR), filtrate exposed to full sunlight (PAR+UVR). However, only 2 replicates per treatment were used for July 10th experiments on Lake Muskoka. Direct overhead sunlight was either blocked or filtered. Acrylic filters were placed approximately 0.5 cm above the PAR and PAR+UVR treatments to regulate light exposure. Filters used were: PAR, OP3 acrylic sheets (Acrylite, 3mm thick, 50% reduction in UV irradiance at 405nm (Vinebrooke & Leavitt 1998)); and PAR+UVR, OP4 acrylic sheets [CYRO Industries, 4.7mm thick, 70–90% transmittance throughout the UVB and UVA range (Kelly et al. 2003)]. A plastic sheet covered with aluminum foil was placed over the shade treatment. All treatments,

including the shade treatment, received indirect sunlight that passed through the translucent polypropylene sides of the incubation containers. The cooling and incubation vessels attenuated approximately 95%, 75%, and 60% of the UVB, UVA, and PAR radiation, respectively (as measured on a Bausch and Lomb 601 Spectronic Spectrophotometer). Samples were incubated outdoors between 11:00–16:00 h in ambient sunlight for approximately 2 h. Containers were suspended in a water bath at ambient lake temperature. PAR and UVR (at 305, 320, 340 nm) exposure of incubation containers was measured with a Biospherical BIC compact 4-channel radiometer (Table 5.1.3). Measurements of solar radiation were not available for July 16th and 18th; therefore total solar radiation (TSR, KJ m⁻²) measurements were obtained from a meteorological field station on the site (Locke & de Grosbois 1986; Gennings et al. 2001).

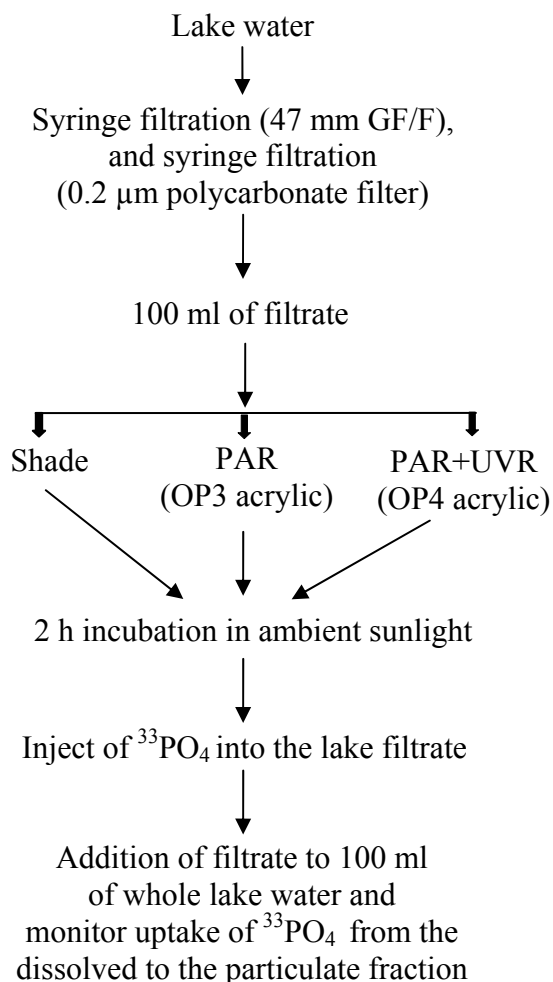


Figure 5.1.1. The experimental protocol used in lake filtrate experiments. Epilimnetic lake water (20 l) was collected 1–2 m below the lake surface. Lake filtrate (<0.2 μm, 100 ml) was subjected to three experimental treatments (shade, PAR, PAR+UV). Incubations were conducted under ambient sunlight (2 h). The turnover time of the phosphate pool was measured after the samples had received one of the three experimental treatments.

At the end of the incubation period all containers were transferred to the laboratory, where carrier-free radiophosphate (³³PO₄, ICN Biomedicals, final activity ~50 000 cpm ml⁻¹, final concentration ~110 pg PO₄ l⁻¹) was injected. This treated and labeled filtrate was then added to containers that contained 100 ml of whole lake water (final volume = 200 ml; 100 ml of whole lake water + 100 ml of lake filtrate). Planktonic uptake of

radiophosphate was monitored for approximately the first 15 min of incubation of the combined water samples by sampling the dissolved pool at approximately 1, 2, 5, 8, and 12 min (syringe filtration, 5- to 10-ml sub-samples, 25-mm diameter polysulphone, 0.2- μm pore size, Cameo). Each vessel was sub-sampled (4 ml) to determine total radioactivity added. Radioactivity was measured by liquid scintillation (Ecolume® counting fluid) and corrected for background radioactivity. Quenching of samples was not detected.

Radioactivity remaining in the dissolved fraction (i.e. total disintegrations per minute) over time was fitted to a polynomial function (Currie & Kalff 1984; Bentzen & Taylor 1991). The polynomial of best fit (by eye) to the initial time series points (e.g., at times equal to 0, 1, 2, and 5 minutes) was used. The uptake constant (k) was determined by taking the derivative of the polynomial at time zero and dividing by the total radioactivity in each incubation vessel (Currie & Kalff 1984; Bentzen & Taylor 1991). The reciprocal of this uptake constant is equal to the turnover time of the dissolved PO_4^{3-} pool.

Water chemistry

Additional water samples (filtrate or whole water (100–200 ml), $n = 2$) were incubated concurrently during each experiment as the PAR+UVR treatment. However, these samples were used to determine the effect of PAR+UVR exposure on the spectral properties of the lake water and on the concentration of DOC. The effect of PAR+UVR on the spectral properties of lake water was examined with spectral absorbance (280–700 nm) at 1nm intervals (Cary 100 UV/VIS Scanning Spectrophotometer). These spectra were then compared to unexposed lake water spectra (exposed-unexposed). The effect of PAR+UVR on the concentration of DOC (mg l^{-1}) was also examined by comparing

unexposed lake water samples to exposed samples. DOC concentration was measured by acidifying samples and flushing with nitrogen gas to remove inorganic carbon (C). Organic C was then oxidized to CO₂ by exposure to UV radiation in acid persulfate media and measured colorimetrically with phenolphthalein using a Technicon auto analyzer (Dillon & Molot 1997).

Analysis for total and dissolved P was measured on the remaining lake water according to (Parsons et al. 1984). The quantity of P in the particulate fraction (>0.2 µm) was determined through subtraction (total P – dissolved P).

Statistical Analysis

The effect of treatment on the turnover time of the dissolved PO₄³⁻ pool was determined with one-way analysis of variance (ANOVA). When significant differences were observed, multiple pairwise comparisons were performed applying Bonferroni correction factors. Differences in spectral absorbance of lake water across the UVB, UVA, and PAR spectrum between exposed and un-exposed samples were determined using Tukey *t*-tests. Treatments were deemed statistically significant at an alpha level of 0.05. Statistical analyses were performed with Statistica v. 6.1 (StatSoft, Inc., Tulsa, Oklahoma).

5.1.3. Results

DOC concentrations were 4.5, 11.2, and 2.5 mg l⁻¹ and total P concentrations were 5.9, 24.9, and 4.8 µg l⁻¹, for Muskoka, Brandy and Plastic L., respectively (Table 5.1.1). The mean vertical attenuation coefficients determined from the slope ln (wavelength (nm) or PAR) vs. depth were 0.917, 2.34, and 0.363 m⁻¹, for PAR, and 10.2, 27.13, and 2.21 m⁻¹, for UVR in Muskoka, Brandy, and Plastic L., respectively (Table 5.1.2). Total PAR

radiation during experimental trials had a range of 3383 to 4399 KJ m⁻² h⁻¹. Total UVR during experimental trials had a range of 422 to 534 KJ m⁻² h⁻¹ (Table 5.1.3).

Table 5.1.3. Total incident solar radiation for each experiment. Photosynthetically active radiation (PAR) and total ultraviolet radiation (UVA+UVB) were obtained from nearby meteorological field stations (Locke & de Grosbois 1986; Gennings et al. 2001).

Lake	Date ddmmyy	PAR (KJ m ⁻² h ⁻¹)	UVR (KJ m ⁻² h ⁻¹)
Muskoka	100707	3383	421.5
	160707	4399	548.1
Brandy	180707	3871	482.3
Plastic	230707	4288	534.3

Lake Muskoka filtrate (<0.2 µm) that was exposed to PAR+UV had greater spectral absorbance throughout the UVB (280–320 nm) and UVA (320–400 nm) spectra, but had reduced absorbance throughout the PAR (400–700 nm) spectrum relative to the absorbance of unexposed samples (Fig. 5.1.2). In contrast, Brandy and Plastic L. filtrate had reduced spectral absorbance throughout the UVB, UVA, and PAR spectrum (Fig. 5.1.2). These observed differences in spectral absorbance were significant for all trials at all wave lengths (UVB, UVA, and PAR) ($p < 0.001$, t -tests) for all lakes. A change in the DOC concentration between exposed and unexposed treatments was not detectable in any of the lakes ($p \geq 0.21$, t -test) (Table 5.1.4). A significant decrease in the specific UV absorbance [Absorbance₂₄₅:DOC concentration (mg l⁻¹)] in the PAR+UV treatments

compared to the shade treatments was only detected in Plastic Lake ($p = 0.035$, t -test) (Table 5.1.4).

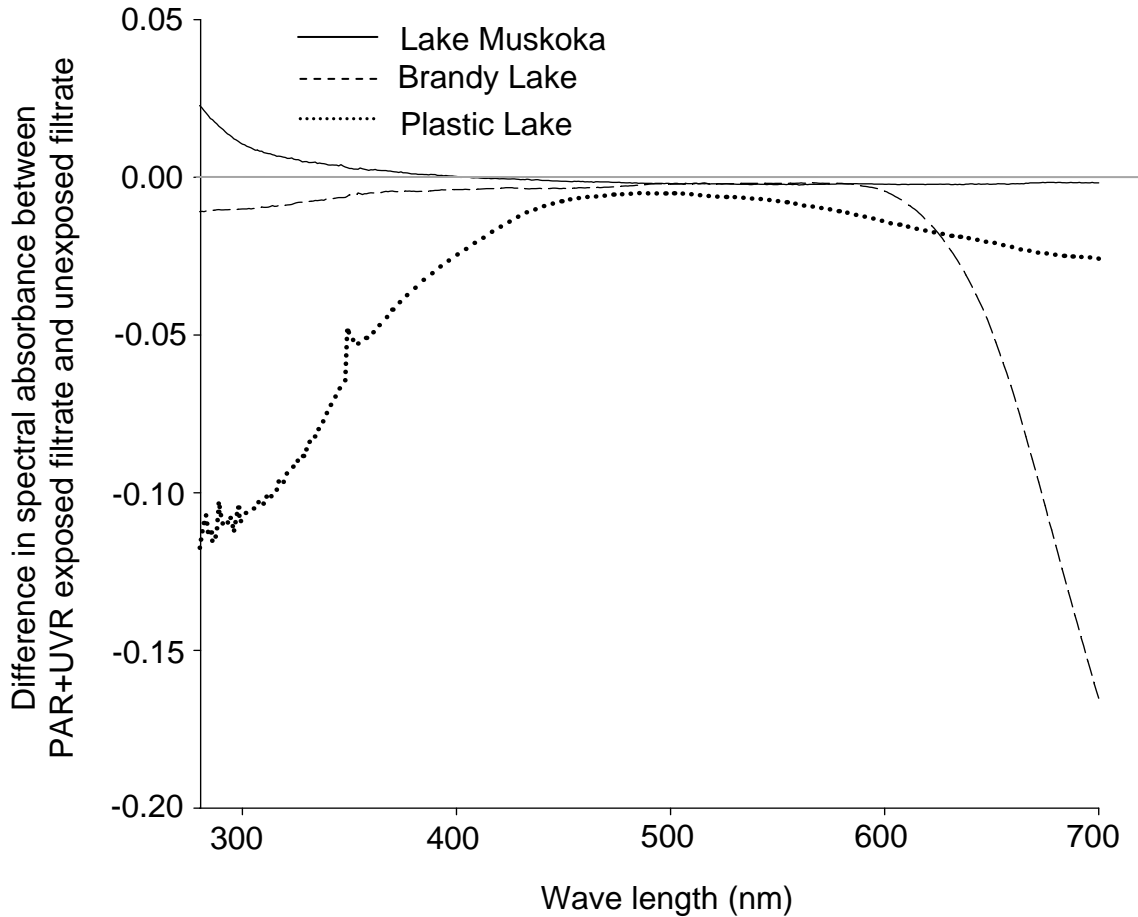


Figure 5.1.2. The spectral absorbance of lake filtrate ($<0.2 \mu\text{m}$) that was exposed (incubated outdoors for 2 h) or unexposed (remained indoors) to direct sunlight. Spectral absorbance was measured at 1 nm wave lengths on a Cary 100 UV/VIS Scanning Spectrophotometer. Differences in the spectral absorbance were significant for all trials at all wave lengths (UVB, UVA, and PAR) ($p < 0.001$, t -test) for all lakes.

Table 5.1.4. Mean dissolved organic carbon (DOC) concentrations (\pm S.E) in the shade and the PAR+UV treatments. Significant changes in DOC concentration following treatment were not detected ($p \geq 0.21$, t -test). Specific UV absorbance (SUVA, Absorbance₂₅₄:DOC concentration) following treatment for each experimental lake are also shown. Larger SUVA ratios indicate a greater number of aromatic compounds in the lake water. A significant decline in SUVA for the PAR+UV treatment compared to the shade treatment was only observed for Plastic L. ($p = 0.035$, t -test)

Lake	Date ddmmyy	DOC (mg l ⁻¹) (shade)	DOC (mg l ⁻¹) (PAR+UV)	SUVA (shade)	SUVA (PAR+UV)
Muskoka	100707	4.29 (0.2)	4.65 (0.7)	0.293 (0.003)	0.293 (0.002)
	160707	4.50 (0.14)	4.40 (0.005)	0.294 (0.004)	0.281 (0.002)
Brandy	180707	11.34 (0.01)	11.30 (0.13)	0.882 (0.001)	0.886 (0.010)
Plastic	230707	2.34 (0.05)	2.73 (0.07)	0.147 (0.005)	0.118 (0.003)

The turnover times of the dissolved PO₄³⁻ pool for PAR+UV treatments were more rapid relative to both shade and PAR treatments for L. Muskoka on July 10th; however, differences were non-significant ($p = 0.18$, $n = 2$, ANOVA) (Fig. 5.1.3). Our second run of this experiment (L. Muskoka, July 16th) with one additional replicate per treatment ($n = 3$) resulted in a significant treatment effect ($p = 0.014$, ANOVA) in the turnover time of the dissolved PO₄³⁻ pool between the shade and the PAR+UV treatment (Fig. 5.1.3). The PAR only treatments on both dates with L. Muskoka filtrate had turnover times that were also more rapid than the shade only treatments (Fig. 5.1.3), but these differences were not significant ($p \geq 0.53$, ANOVA). An effect of PAR+UV or PAR treatment on lake filtrate from Brandy and Plastic Lakes was not detected ($p \geq 0.15$, ANOVA).

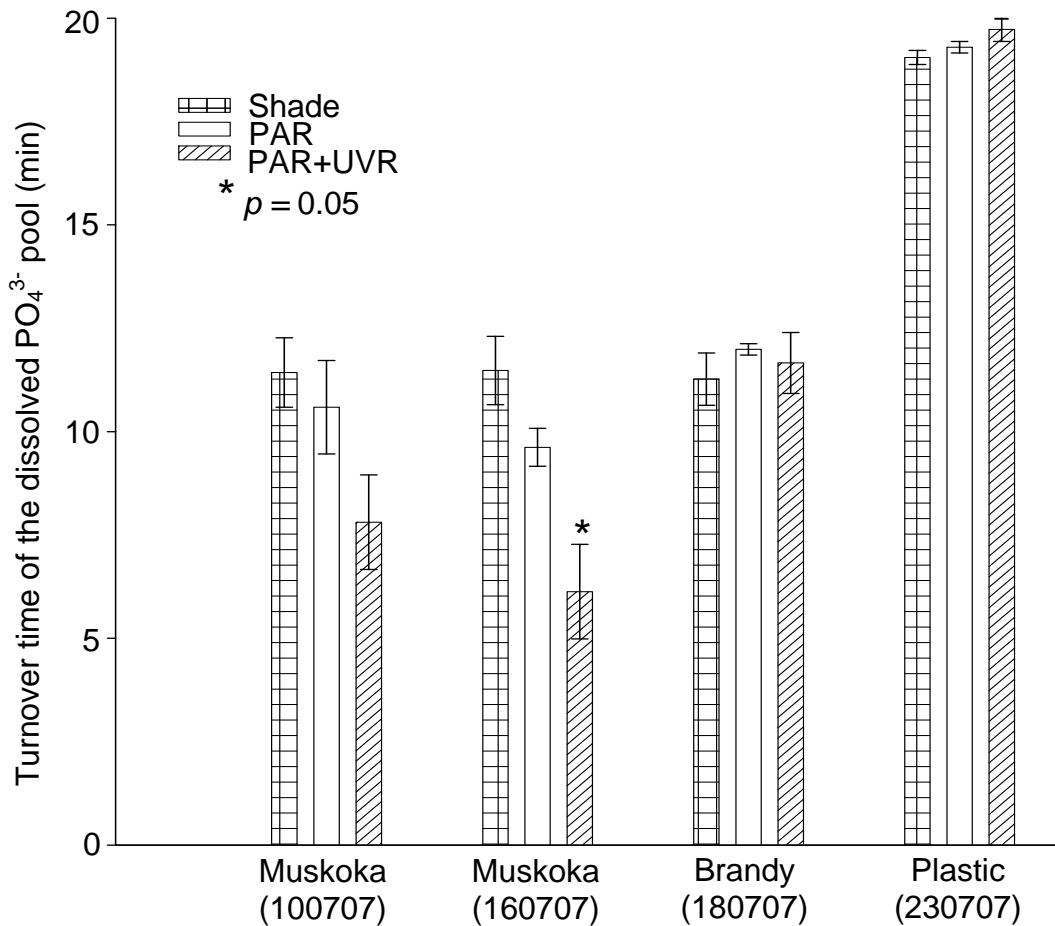


Figure 5.1.3. Lake filtrate ($<0.2 \mu\text{m}$) was subjected to three experimental treatments; shade, PAR, and PAR+UV. The turnover time of the phosphate pool (min \pm 1 S.E) was measured after treatment. Treatment effects were analyzed with one-way ANOVA. When treatment effects were observed ($p < 0.05$) pairwise comparisons with Bonferroni corrections were performed. The turnover time of the phosphate pool in the PAR+UV treatment was significantly less than the shade and PAR treatments, but only for Muskoka and only on one date (July 16th).

5.1.4. Discussion

Turnover times of the PO_4^{3-} pool in the shade treatments of our study lakes were about 3–5 min (unpublished data). A turnover time of 1–30 min is indicative of P-limitation (Lean & Nalewajko 1979; Lean & Pick 1981). We therefore expect that the plankton in our study lakes should be sensitive to changes in PO_4^{3-} concentration, and that changes in

PO_4^{3-} concentration should be detectable by a change in the turnover time of the PO_4^{3-} pool (i.e., the turnover time of the PO_4^{3-} pool should increase as the size of the dissolved PO_4^{3-} pool increases).

A change in turnover was undetectable in PAR+UVR exposed samples from Brandy L. (Fig. 5.1.3) suggesting a change in PO_4^{3-} concentration did not occur. This is contrary to what we would predict based on the findings of Koenings and Hooper (1976), Francko and Heath (1982), and Francko (1986). For example, we would anticipate that photo-labile dissolved humic matter (DHM)-Fe-P complexes would have been present in Brandy L. as a result of the relatively high concentrations of DOC, Fe, and TP (Table 5.1.1). Organically complexed Fe^{3+} readily forms soluble complexes with PO_4^{3-} (Koenings & Hooper 1976; Francko & Heath 1982). Phosphate may be released from these DOM-Fe-P complexes through photo-reductive processes (Koenings & Hooper 1976; Francko & Heath 1982; Francko 1986). However, a detectable increase in free PO_4^{3-} may be dependent on the rate of UV-mediated Fe^{3+} reduction. For example, Francko and Heath (1982) reported that the UV-mediated release of orthophosphate from DOM-Fe complexes was equal to the first order rate of the photoreduction of Fe^{3+} to Fe^{2+} . Photoreductive rates of Fe^{3+} decline markedly as pH rises above 7 (Emmenegger et al. 2001; Scully et al. 2003). Brandy was the least acidic of our study lakes (pH = 7.2); thus low rates of Fe^{3+} reduction may have resulted in PO_4^{3-} remaining complexed with Fe^{3+} .

Similar to Brandy L., Plastic L. did not respond to treatment (Fig. 5.1.3). Plastic L. had low concentrations of DOC, Fe, P and NO_3^- (Table 5.1.1). As such, the chemistry of

Plastic L. may not have been amenable to photo-chemical changes that would influence PO_4^{3-} concentrations at levels detectable by our bioassay.

Turnover time of the PO_4^{3-} pool was more rapid for PAR+UVR treatments relative to shaded and PAR treatments in L. Muskoka (Fig. 5.1.3). The more rapid turnover of the PO_4^{3-} pool suggests that PO_4^{3-} availability decreased in the lake filtrate following exposure to PAR+UVR. We propose that an increase in Fe^{3+} concentration may have resulted in an increase in binding of Fe with PO_4^{3-} resulting in insoluble and unreactive complexes (Perezruiz et al. 1984; Mauzerall et al. 1993; Kopacek et al. 2005).

While ferric iron is routinely the dominant species of Fe present in oxygenated waters, low concentrations of Fe^{2+} may be present (Osullivan et al. 1991; Emmenegger et al. 2001). Fe^{2+} may be effectively oxidized by photochemically produced reactive oxygen species (ROS) (Jayson et al. 1972; Miller et al. 1995; Voelker et al. 1997; Emmenegger et al. 1998). Nitrate (NO_3^-) may be a significant source of hydroxyl radicals through photolytic processes in natural waters (Zafiriou & True 1979; Mack & Bolton 1999). Nitrate concentrations in L. Muskoka ($\sim 172 \mu\text{g l}^{-1}$) (Table 5.1.1) were much greater than in Brandy and Plastic Lakes. In Muskoka ROS production may have been substantial enough to effectively increase Fe^{3+} concentrations through the oxidation of Fe^{2+} .

Although total Fe concentrations were low ($\sim 31 \mu\text{g l}^{-1}$) in L. Muskoka, steady state phosphate concentrations (Hudson et al. 2000) in L. Muskoka were only $\sim 284 \text{ pM l}^{-1}$ (unpublished data). As such, only a marginal increase in the concentration of Fe^{3+} may have been required to sequester enough free PO_4^{3-} to induce the observed response (Fig. 5.1.3). A similar mechanism has been proposed by Scully et al. 2003)

whereby free Fe^{2+} is oxidized by photochemically produced H_2O_2 and subsequently binds to, and inactivates, alkaline phosphatase.

Despite the short incubation times (2 h) changes in the absorptive properties of the PAR+UVR exposed filtrate were observed (Fig. 5.1.2). PAR+UVR exposed filtrate in Lake Muskoka attenuated solar radiation more strongly throughout the UV spectrum (Fig. 5.1.2). Maloney et al. (2005) reported that the oxidation of Fe^{2+} resulted in a greater absorption of solar radiation within the UV spectrum. As such, the observed increase in spectral absorbance may provide indirect support for our hypothesis that Fe^{3+} concentrations had increased in PAR+UV exposed samples in Muskoka L. water. However, in Brandy and Plastic Lakes the opposite effect was observed, with a reduction in the absorption of solar radiation in the PAR+UVR exposed samples (Fig. 5.1.2). This suggests that increases in Fe^{3+} did not occur and Fe^{3+} may not be binding to PO_4^{3-} as in Muskoka; hence no change in turnover. Francko and Heath (1982) have reported a linear relationship between decreases in absorbance at 400nm and increases in PO_4^{3-} concentration. Although absorbance at 400nm decreased in the PAR+UV exposed filtrate in both Brandy and Plastic Lakes, a change in PO_4^{3-} concentration was not observed.

In summary, we have used turnover time of the PO_4^{3-} pool as a bioassay to determine if a change in PO_4^{3-} concentration occurred in lake water filtrate exposed to PAR+UV. Although, a shift in spectral absorbance was always detectable in PAR+UV exposed samples, a concomitant change in the concentration of PO_4^{3-} was not observed. In fact, L. Muskoka was the only lake to respond to treatment, with an apparent decrease in PO_4^{3-} availability. We propose that a ROS mediated increase in Fe^{3+} concentration may have resulted in free PO_4^{3-} being sequestered into insoluble and unreactive Fe-P complexes.

Although, we did not directly test this hypothesis, an increase in the spectral absorbance throughout the UVR spectrum of PAR+UVR exposed filtrate may provide indirect evidence. However, further research is required to elucidate the generality of this response, as well to determine under what conditions UVR exposure may result in an increase in the concentration of free PO_4^{3-} .

5.2. Generality of the Response of Dissolved Organic Phosphorus to Ultraviolet Radiation

5.2.1. Introduction

Early studies (e.g., Francko & Heath 1979,1982) reported that substantial quantities of PO_4^{3-} may be released from DHM-Fe-P complexes following UVR irradiance. However, I suspect that detectable amounts of PO_4^{3-} may not be released from dissolved organic compounds during UVR exposure in lakes when concentrations of Fe^{3+} and humic substances in the epilimnion are low (Cotner & Heath 1990; Vahatalo et al. 2003). Moreover, I have demonstrated that concentrations of PO_4^{3-} may actually decline in lake filtrate ($<0.2 \mu\text{m}$) that is exposed to UVR. However, the generality of any one response (i.e., an increase or decrease in P availability) is unclear and further experimentation across a diverse set of lakes is warranted.

5.2.2. Methods

The methods for this set of experiments follow that of previous experiments (Fig. 5.1.1, Section 5.1.2) with the following changes. Surface water ($\sim 20 \text{ l}$) was collected from 10 lakes located in Saskatchewan, Canada (Table 5.2.1). Samples (200 ml) were incubated outdoors (between 9:00–16:00 h) in ambient sunlight for approximately 6 h. Solar radiation was measured with an Ocean Optics USB 2000 radiometer.

5.2.3. Results

DOC concentrations had a range of 5.3 to 41.4 mg l⁻¹ (Table 5.2.1). Total P concentrations had a range of 13.3 to 64.8 µg l⁻¹. Total Fe concentrations had a range of 8.8 to 112.5 µg l⁻¹, and nitrate concentrations had a range of 0.05 to 1.95 mg l⁻¹. Total PAR radiation received by experimental trials had a range of 632 to 2734 (1865 ± 775, mean ± 1 S.D.) (KJ m⁻² h⁻¹). Total UVR received by experimental trials had a range of 87 to 322 (236 ± 77, mean ± 1 S.D.) (KJ m⁻² h⁻¹) (Table 5.2.2).

The average molecular weight of DOC (inferred from absorbance ratio 250:365 nm) and the specific UV absorbance [Absorbance₂₄₅:DOC concentration (mg l⁻¹)] decreased in the PAR+UVR exposed lake filtrate (<0.2 µm) (Table 5.2.3). An effect of PAR treatment on the absorbance ratio 250:365 nm or on the specific UV absorbance of DOC was not observed.

The liberation of PO₄³⁻ from DOP was not detected in the PAR+UVR treatment ($p \geq 0.11$), except for one lake (Upper Blackstrap L.). The turnover time of the dissolved PO₄³⁻ pool for the PAR+UVR treatment was significantly greater than the shade (control) treatment for Upper Blackstrap L. filtrate ($p = 0.01$) (Fig. 5.2.1). The turnover time in the PAR+UVR treatment for Torch L. [mean = 6.75±1.65 (SD)] was also greater than the turnover time of the shade treatment [mean = 4.32±0.45 (SD)] (Fig. 5.2.1) although this difference was non-significant ($p = 0.11$). An effect of the PAR treatment on lake filtrate was not detected in any of the lakes.

Table 5.2.1. Physical and chemical properties of the study lakes at the time of sampling.

Lake	Date (ddmmyy)	Latitude (°N)	Longitude (°W)	pH	TP (µg l ⁻¹)	TDP (µg l ⁻¹)	DOC (mg l ⁻¹)	Fe (µg l ⁻¹)	Nitrate (mg l ⁻¹)	Chl <i>a</i> (µg l ⁻¹)
Emerald	120707	53°11'	106°57'	8.6	13.3	4.0	19.2	38.8	0.478	2.4
Diefenbaker	280608	51°14'	106°51'	7.65	13.4	4.7	5.3	71.3	1.948	3.7
Memorial	140708	53°17'	107°03'	8.79	19.6	10.1	26.2	46.3	0.109	5.4
Constance	290808	53°10'	106°58'	8.72	24.8	5.0	41.4	112.5	0.053	1.1
Pinkney	120808	54°02'	105°04'	7.69	26.9	12.7	13.5	8.8	0.059	1.9
Iroquois	220708	53°09'	107°02'	8.72	30.0	17.5	18.2	28.8	0.075	2.0
Torch	010808	53°44'	105°16'	8.0	46.6	27.6	23.5	112.5	0.136	8.1
Upper Blackstrap	250808	50°53'	106°26'	7.90	47.1	25.7	6.6	60.0	0.130	6.7
Murray	070808	53°02'	108°16'	8.04	64.8	24.3	13.8	27.5	0.311	13.6

Table 5.2.2. Total incident solar radiation received by each experimental trial. Solar radiation measurements ($\text{KJ m}^{-2} \text{h}^{-1}$) were taken with an Ocean Optics USB2000 radiometer. Values have been corrected for attenuation by acrylic filters. nd = no data available

Lake	Date (ddmmyy)	PAR	Total UVR	UVA	UVB
Emerald	120707	nd	nd	nd	nd
Diefenbaker	280608	992.5	87.3	86.4	0.87
Memorial	140708	2719	266.5	256.2	10.3
Lac la Pêche	090708	1868	219.2	210.6	8.6
Constance	290808	2677	344.1	332.6	11.4
Pinkney	120808	1022	185.9	176.0	9.9
Iroquois	220708	632.2	181.5	169.1	12.4
Lower Blackstrap	280708	1864	265.0	250.8	14.3
Torch	010808	2734	322.6	312.7	9.9
Upper Blackstrap	250808	1762	200.2	195.2	5.0
Murray	070808	2377	288.1	280.2	7.9

Table 5.2.3. The absorbance ratio 250:365 nm in lake filtrate exposed to one of two experimental treatments (shade or PAR+UVR) for 6 h. Larger numbers indicate a decrease in the average molecular weight. Specific UV absorbance (SUVA, Absorbance₂₅₄:DOC concentration) following treatment for each experimental lake are also shown. Larger SUVA ratios indicate a greater number of aromatic compounds in the lake water. Numbers in bold indicate differences between shade and PAR+UVR treatments are significant at an alpha level of 0.05.

Lake	absorbance ratio 250:365 nm		SUVA	
	Shade	PAR+UVR	Shade	PAR+UVR
Emerald	16.68	17.85	0.116	0.116
Diefenbaker	8.42	8.98	0.187	0.184
Memorial	15.12	16.95	0.117	0.116
Constance	24.87	24.21	0.049	0.49
Pinkney	9.93	10.43	0.162	0.158
Iroquois	15.91	17.14	0.106	0.105
Upper Blackstrap	24.5	16.58	0.153	0.149
Lower Blackstrap	7.15	8.30	0.106	0.104
Torch	9.87	10.67	0.226	0.223
Murray	10.50	11.49	0.201	0.193

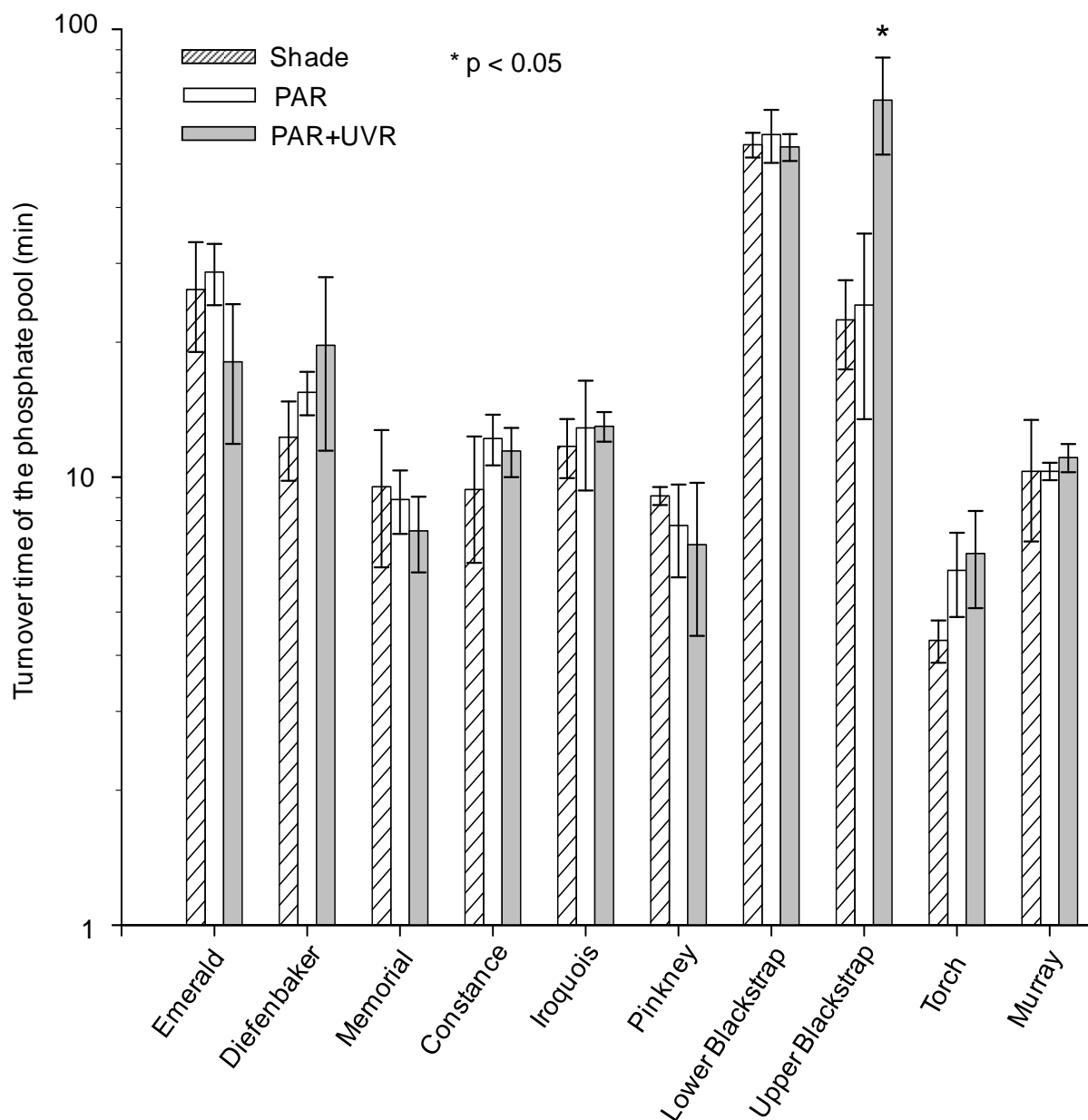


Figure 5.2.1. Turnover time of the dissolved phosphate pool ($\text{min} \pm 1 \text{ S.D.}$) after lake filtrate ($<0.2 \mu\text{m}$) was exposed to the experimental treatments: shade, PAR, or PAR+UVR. The turnover time of the phosphate pool was significantly greater for Upper Blackstrap L. Treatment effects were analyzed with one-way ANOVA. When treatment effects were observed ($p < 0.05$) Dunnet's pairwise comparisons (applying Bonferroni correction factors) with the control (shade treatment) were performed. Lakes increase in total P from left to right.

5.2.4. Discussion

Despite the short incubation times (6 h), photochemical changes in the mean absorbance ratio (250:365 nm) and specific UV absorbance (SUVA, Absorbance₂₅₄:DOC concentration) were observed (Table 5.2.3). Photochemical modification of DOP may increase PO₄³⁻ availability (Francko & Heath 1982; Wetzel et al. 1995; Vahatalo et al. 2003). However, a significant ($p < 0.05$) change in the turnover time of the PO₄³⁻ pool in the PAR+UVR treatment was undetectable except for one lake (Upper Blackstrap) (Fig. 5.2.1). Moreover, we did not detect a decrease in PO₄³⁻ availability as was observed for L. Muskoka (Fig. 5.1.2) (Sereda et al. 2009).

The turnover time in the PAR+UVR treatment for Upper Blackstrap L. was greater than in the shade treatment indicating that the size of the dissolved P pool had increased (Fig. 5.2.1). Upper Blackstrap L. is shallow ($z = 3$ m) and polymictic. On the day of sampling the lake was well mixed (average wind speed during time of sampling ~ 26 km h⁻¹, http://www.climate.weatheroffice.ec.gc.ca/climateData/hourlydata_e.html) with a substantial amount of lake sediment suspended in the water column (sediment was also observed settled on the bottom of the collection vessel, personal observation). We suspect that photosensitive DOP compounds may have been released from the lake sediments into the water and that PO₄³⁻ was liberated from the DOP upon irradiation. Torch Lake is similarly shallow ($z = 1.5$ m) and polymictic. As with Blackstrap L., sediments were suspended in the water column and settled on the bottom of our collection vessel (personal observation). The turnover times in the PAR+UVR treatment [mean = 6.75 ± 1.65 (SD)] were also greater than the turnover times of the shade treatment [mean = 4.32 ± 0.45 (SD)] (Fig. 5.2.1), although these differences were non-significant ($p = 0.11$)

for Torch Lake. We hypothesize that photosensitive DOP compounds may be released from lake sediments and liberate PO_4^{3-} upon irradiation on windy days; however, further experimentation is required to confirm this.

The absence of a UVR effect on the concentration of the dissolved PO_4^{3-} pool in the majority of our lakes may have come about from a lack of photosensitive DOP compounds in the water column of our lakes. For example, the presence of Fe^{3+} and dissolved humic substances (DHS) in the epilimnion may be necessary for the photodecomposition of UV-sensitive P compounds (Cotner & Heath 1990; Francko 1986). Both Cotner and Heath (1990) and Vahatalo et al. (2003) have demonstrated that lakes with low concentrations of Fe^{3+} and DHS may not generate detectable concentrations of PO_4^{3-} through photodecomposition processes. Concentrations of DHS were low in the majority of our study lakes (see SUVA values, Table 5.2.3), and consequently, photo-reactive DHS-Fe-P complexes may have been in very low concentration or absent.

Zhou (1996) has suggested that the presence of oxidizing agents such as photochemically produced hydroxyl radicals may also be important in the release of photosensitive P from DOP. Hydroxyl radical production may occur through the photolysis of nitrate (NO_3^-) (Zellner et al. 1990; Mack & Bolton 1999) and photo-Fenton reactions in lakes with high concentrations of DOM and Fe (Zepp et al. 1992; White et al. 2003; Molot et al. 2005). However, the rate of radical production through either pathway is pH dependent, with radical yields decreasing with increasing pH (Zellner et al. 1990; Zepp et al. 1992; Molot et al. 2005). Consequently, the production of PO_4^{3-} from DOP may be dependent on lake chemistry (i.e., concentrations of DOM, Fe, NO_3^- , TP, and

pH). Despite our study lakes encompassing a broad range in DOC, Fe, NO_3^- and TP (Table 5.2.1) our lakes were neutral to basic (pH 7.5–8.9) with DOC in only 5 of the 10 study lakes exhibiting significant photochemical degradation (Table 5.2.3). Therefore, it may be that radical production was insufficient to result in a detectable release of PO_4^{3-} from DOP. Nonetheless, our study includes a diverse set of lakes and demonstrates that the photodecomposition of DOP to PO_4^{3-} is not a significant P pathway in the surface water of lakes.

5.3. Biotic Effects⁶

5.3.1. Introduction

Phosphorus (P) is supplied to primary producers during the growing season predominantly through regenerative processes within the plankton assemblage (Hudson et al. 1999; Sereda et al. 2008). This rapid recycling of nutrients may be essential to sustaining primary productivity in both freshwater and marine environments. Consequently there has been much interest in understanding the physical, chemical and environmental factors that influence P cycling. For example, a vast amount of research has been conducted on the implications of ultraviolet radiation (UVR) on planktonic nutrient acquisition (Dohler & Biermann 1987; Behrenfeld et al. 1995; Allen & Smith 2002; Aubriot et al. 2004). It has been demonstrated that the uptake of P may be suppressed (Allen & Smith 2002; Frost & Xenopoulos 2002; Aubriot et al. 2004) or stimulated by UVR (Aubriot et al. 2004) under elevated P concentrations. However, an effect of UVR on the uptake of P was not observed at ambient phosphate (PO_4^{3-}) concentrations by these past studies (Allen & Smith 2002; Frost & Xenopoulos 2002). While the interactive effects of UVR and P additions may be of interest, more

⁶ Contents of this chapter have been published in *Hydrobiologia*. 2011. **665**: 205–217.

information is required to understand the significance of UVR in altering plankton P cycling at ecologically relevant PO_4^{3-} concentrations (i.e., picomolar concentrations). Past research has been limited to a few individual systems (Allen & Smith 2002; Aubriot et al. 2004), prolonged incubations in bags (Frost & Xenopoulos 2002; Xenopoulos et al. 2002) or lab cultures (Hessen et al. 2008). It may be that experimentation with natural plankton assemblages across broader environmental and/or chemical gradients is required to understand how UVR may alter P kinetics at ambient PO_4^{3-} concentration.

It has been suggested that the apparent lack of response of P uptake to UVR irradiance at ambient PO_4^{3-} concentration observed in past studies may be a result of both the specific uptake rate and the ambient concentration of dissolved PO_4^{3-} having been reduced, such that a change in the specific uptake (turnover) was undetectable (Allen & Smith 2002). This may be possible if the regeneration rate of dissolved P decreased more than the specific uptake rate. While conceptually possible, the effect of UVR on the regeneration of dissolved P remains unknown. Furthermore, a change in P uptake and/or in the regeneration of dissolved P under UVR irradiance should, in-turn, alter PO_4^{3-} concentrations. However, the effect of UVR on ambient PO_4^{3-} concentrations has not been investigated. This gap in our knowledge is disconcerting given the significance of regenerative processes in supplying P to primary producers (Hudson et al. 1999; Sereda et al. 2008) and further investigation is warranted.

The dissolved organic P (DOP) pool may be a significant source of phosphorus (P) when the dissolved inorganic P (DIP) pool becomes depleted (Cotner & Wetzel 1992; Thingstad et al. 1993; Monaghan & Ruttenberg 1999; Cavender-Bares et al. 2001; Nausch & Nausch 2004). Phosphate concentrations may be augmented by alkaline

phosphatase activity (APA), and offset potential UVR induced declines in dissolved P regeneration. However, APA may be inactivated by UVR (Garde & Gustavson 1999; Tank et al. 2005). If APA is inactivated by UVR, and APA is a significant source of PO_4^{3-} to the dissolved PO_4^{3-} pool, then a decrease in the ambient concentration of dissolved PO_4^{3-} would be expected in UVR exposed samples. In turn, a reduction in the dissolved PO_4^{3-} pool would be expected to result in a decrease in the turnover time of the PO_4^{3-} pool. However, simultaneous measurements of APA and PO_4^{3-} uptake in UVR exposed planktonic assemblages are not available to test this hypothesis.

Several gaps exist in our knowledge on the effects of UVR on pelagic P cycling. Until these gaps are filled, our ability to predict the impact of UVR on limnetic systems may be limited. Therefore our study first aimed to determine if and how UVR may affect the turnover time of the dissolved PO_4^{3-} pool in natural plankton assemblages [at ambient (picomolar) concentrations] across broad environmental and chemical gradients. Second we aimed to assess how UVR may alter phosphatase activity and, determine if a change in APA under UVR irradiance is correlated with a change in P uptake as proposed in the literature. Third, we aimed to assess the influence of UVR on the regeneration of dissolved P, the turnover rate of particulate P, and on PO_4^{3-} concentrations. We expect that a change in P uptake, the regeneration of dissolved P and/or APA should in turn influence ambient PO_4^{3-} concentrations.

5.3.2. Methods

The effects of UVR exposure on P cycling was examined in 18 thermally stratified or polymictic lakes located in Ontario and Saskatchewan, Canada (Table 5.3.1). Lakes were sampled once during 2007, 2008 or 2010 (June through August).

Surface lake water (~20 l) was collected 1–3 m below the surface from a central location with a Van Dorn (Fig. 5.3.1a and b, step 1). Water was gently decanted into a collapsible polyethylene bag. All experimental containers were washed (0.1% Liqui-Nox P-free detergent), leached (0.1M HCl), and rinsed with lake water (polyethylene bag), or distilled water (incubation containers). Surface water temperature was recorded and water samples were transported to the laboratory in a cooler.

Lake water (200–500 ml) was gently transferred into pre-washed open-top polypropylene containers (Starfrit®, 350–850 ml) (Fig 5.3.1a, step 2). Three treatments (replicate incubation vessels, $n = 3$) were established (Fig. 5.3.1a, step 3): lake water exposed to low intensity indirect sunlight (control), lake water exposed to photosynthetically active radiation only (PAR), and lake water exposed directly to PAR+UVR. Direct overhead sunlight was either blocked or filtered. Acrylic filters were placed approximately 0.5 cm above the PAR and PAR+UVR treatments to regulate light exposure. Filters used were: PAR, OP3 acrylic sheets [Acrylite, 3 mm thick, 50% reduction in UVR irradiance at 405 nm (Vinebrooke & Leavitt 1998)]; PAR+UVR, OP4

Table 5.3.1. Physical and chemical properties of the study lakes at the time of sampling. Note, Muskoka and Brandy Lakes are located in central Ontario, Canada. All other study lakes are located in Saskatchewan, Canada. nd = no data available

Lake	Date (ddmmyy)	pH	TP ($\mu\text{g l}^{-1}$)	TDP ($\mu\text{g l}^{-1}$)	DOC (mg l^{-1})	Chl <i>a</i> ($\mu\text{g l}^{-1}$)	Specific conductivity ($\mu\text{S cm}^{-1}$)	Temperature ($^{\circ}\text{C}$)	Mixing depth (m)	Max depth (m)
Muskoka	160707	6.7	5.9	3.8	4.5	nd	nd	20.0	4.5	28
Emerald	120707	8.6	13.3	4.0	19.2	2.4	1367	22.0	6.0	12.5
Memorial	140708	8.79	19.6	10.1	26.2	5.4	1735	19.9	5.0	5.0
Lac la Pêche	090708	8.51	21.2	8.2	12.9	14.2	434	19.7	5.5	13.0
Delaronde	260710	7.98	21.6	6.9	14.4	4.7	456	22.5	4.2	4.2
Constance	290808	8.72	24.8	5.0	20.6	1.1	852	18.0	6.7	22.3
Brandy	180707	7.02	24.9	14.2	11.2	nd	nd	20.0	2.5	7.5
Pinkney	120808	7.69	26.9	12.7	13.5	1.9	129	20.0	12.5	12.5
Turtle	050808	8.06	28.9	6.3	18.3	7.8	534	18.7	14	14
Iroquois	220708	8.72	30.0	17.5	18.2	2.0	601	21.2	16	16
Little Loon	050808	8.66	34.4	9.7	15.3	7.9	508	18.6	10	10

Upper Blackstrap	280708	7.92	37.5	12.7	6.6	17.3	730	21.4	6.5	6.5
Lower Blackstrap	280708	7.97	40.8	15.5	7.3	11.6	887	21.4	6.5	6.5
Pelletier	010808	8.94	41.7	14.7	13.0	19.5	742	19.9	9.0	9.0
Torch	010808	8.0	46.6	27.6	23.5	8.1	242	19.9	1.6	1.6
Murray	070808	8.04	64.8	24.3	13.8	13.6	1004	19.4	9.0	9.0
Wildlife Pond	230608	8.07	76.3	25.6	36.3	0.43	3639	22.4	1.5	1.5
Cowan	260710	7.2	102.7	68.9	14.6	6.8	602	18.0	5.5	5.5

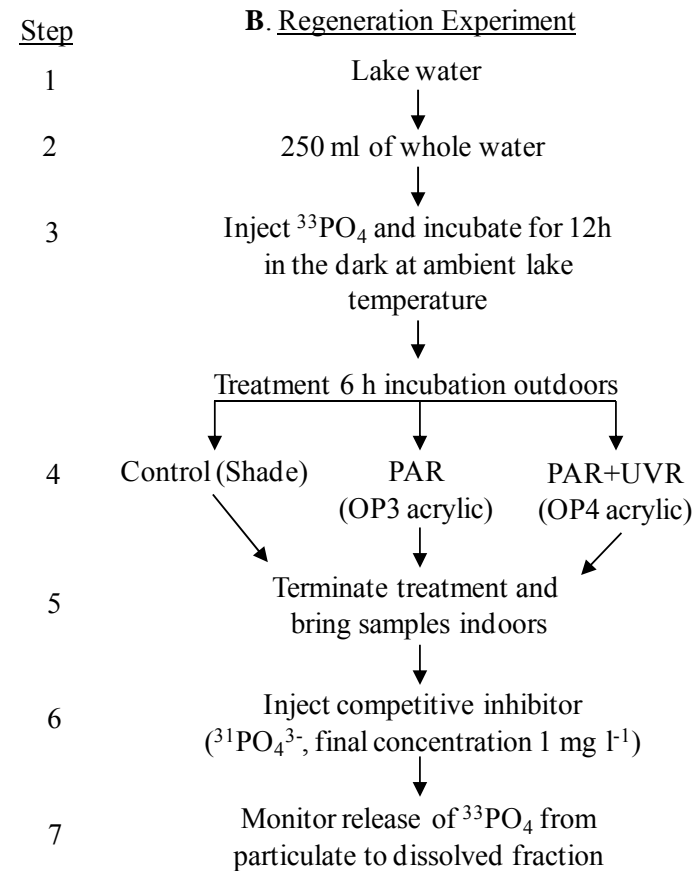
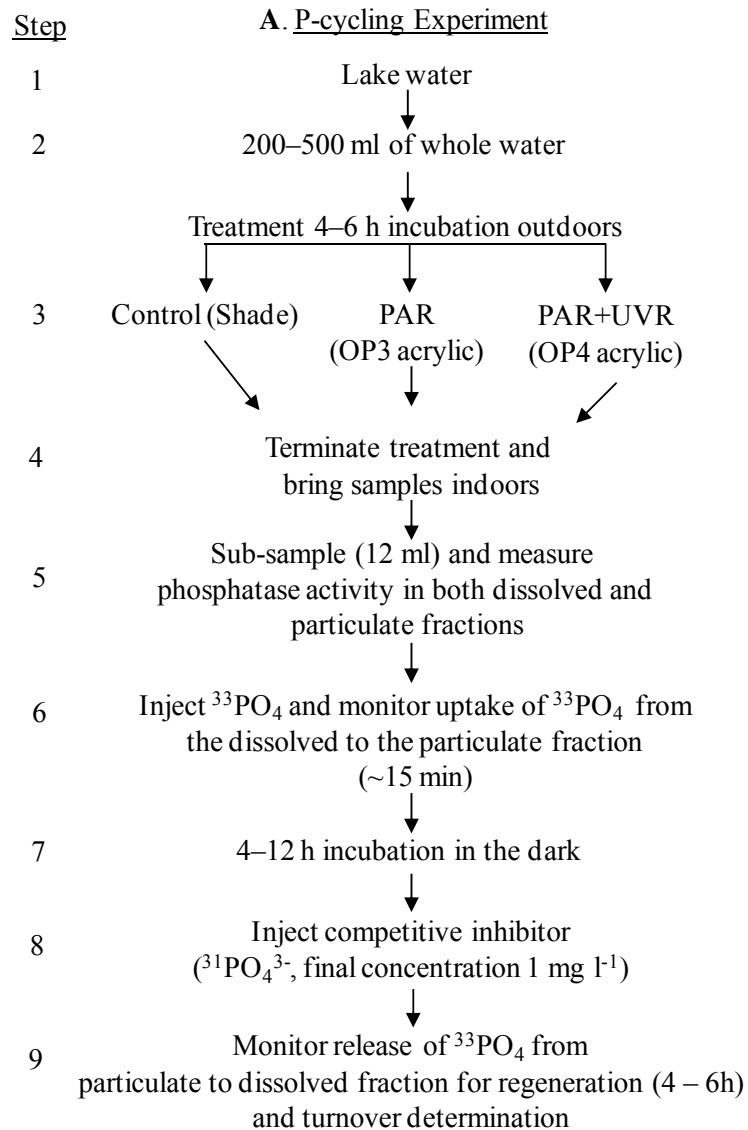


Figure 5.3.1. The experimental protocol. Surface lake water (20 l) was collected 1–3 m below the lake surface. Lake water (200–500 ml) was subjected to three experimental treatments (control, PAR, PAR+UVR). Incubations were conducted under sunlight (4–6 h). Triplicate incubation vessels ($n = 3$) were used for each set of controls and treatments.

acrylic sheets [CYRO Industries, 4.7 mm thick, 70–90% transmittance throughout the UVB and UVA range (Kelly et al. 2003)]. An aluminum foil covered plastic sheet was placed over the shade treatment (here after referred to as the ‘control’). Samples were incubated outdoors (between 9:00–16:00 h) for approximately 4–6 h (Fig. 5.3.1a, step 3). Containers were suspended in a water bath at ambient lake temperature. The sides of the water bath were covered with aluminum foil so incubation vessels only received down-welling radiation. Measurements of total solar radiation (TSR and total UVR, $\text{KJ m}^{-2} \text{h}^{-1}$) during the 2007 experiments were obtained from nearby meteorological field stations (Table 5.3.2). Solar radiation was measured with an Ocean Optics USB 2000 radiometer during the experiments in the summer of 2008 and 2010. Solar radiation received by each incubation vessel was corrected for attenuation by the filters. At the end of the incubation containers were brought into the laboratory and sub-sampled (12 ml) to measure alkaline phosphatase activity (APA) (Fig. 5.3.1a, steps 4 and 5). The turnover time of the dissolved PO_4^{3-} pool was then measured (Fig. 5.3.1a, step 6).

Effect of UVR on APA

Directly after lake water was incubated sub-samples were collected to measure whole water (2 ml) and dissolved (10 ml - syringe filtration, 25 mm diameter polysulphone, 0.2 μm pore size, Cameo) APA activity. Then 2 ml of each sub-sample was placed into individual wells on a multi-well fluorometer plate (Falcon). Next, 0.5 ml of 4 mM 4-methylumbelliferyl phosphate (MU-P) stock solution (MP Biomedicals 102359) in TRIS

buffer (50 mM, Alfa Aesar A18494) that was adjusted to a pH of 8 with HCl was added (Pettersson & Jansson 1978). The hydrolysis of MU-P to methylumbelliferyl (MU) was monitored at regular time intervals with a fluorometer (Varioskan Flash Fluorometer) (excitation 368 nm, emission 448 nm). A negative control [deionized water + methylumbelliferyl phosphate (MP Biomedicals 152475)] and a quench standard (lake water + methylumbelliferyl) were run simultaneously to correct for spontaneous hydrolysis of methylumbelliferyl phosphate in our samples. Phosphatase activity in the particulate fraction was determined through subtraction (whole water activity – filtrate activity). Phosphatase activity was standardized for plankton biomass (measured as particulate P) ($\text{APA nm l}^{-1} \text{ h}^{-1} \div \text{particulate P } \mu\text{g l}^{-1}$).

Effect of UVR on the Turnover Time of the PO_4^{3-} Pool

After sub-sampling for APA, carrier-free radiophosphate ($^{33}\text{PO}_4$, ICN Biomedicals, final activity $\sim 50\,000 \text{ cpm ml}^{-1}$, final concentration $\sim 110 \text{ pg PO}_4 \text{ l}^{-1}$) was injected into the lake water in each of the control and treatment vessels (Fig. 5.3.1a, step 6). Planktonic uptake of radiophosphate was monitored for approximately the first 15 min of incubation by sampling the dissolved pool at approximately 1, 2, 5, 8, and 12 min (syringe filtration, 5 to 10 ml sub-samples, 25 mm diameter polysulphone, 0.2 μm pore size, Cameo). Each vessel was sub-sampled (2–4 ml) to determine total radioactivity added. Radioactivity was measured by liquid scintillation (Ecolume® counting fluid) and corrected for background radioactivity (activity of unlabeled water). Quenching of samples was not detected.

Radioactivity remaining in the dissolved fraction (i.e., total disintegrations per minute) over time was fitted to a polynomial function (Currie & Kalf 1984; Bentzen & Taylor

1991). The polynomial of best fit (by eye) to the initial time series points (e.g., at times equal to 0, 1, 2, and 5 minutes) was used (Bentzen & Taylor 1991). The uptake constant (k) was determined by taking the derivative of the polynomial function at time zero and dividing by the total radioactivity in each incubation vessel (Currie & Kalf 1984; Bentzen & Taylor 1991). Coefficients of determination for uptake curves were ≥ 0.99 , except for Upper Blackstrap L. where R^2 values for uptake curves in the UVR treatment were ≥ 0.96 (see Appendix 5.3.2 for an example). The reciprocal of this uptake constant is equal to the turnover time of the dissolved PO_4^{3-} pool.

The remaining water in each incubation vessel was incubated in the dark at ambient lake temperature for an additional 4–12 h to label the planktonic assemblage (Fig. 5.3.1a, step 7). Samples were incubated in the dark to prevent light-induced repair mechanisms (e.g., photo-enzymatic repair) which may reduce our ability to detect a treatment effect. Then these incubations were terminated with the addition of unlabelled $^{31}\text{PO}_4^{3-}$ as a competitive inhibitor (final concentration 1 mg l^{-1}) (Hudson & Taylor 1996) to prevent further uptake of radiophosphate (Fig. 5.3.1a, step 8). Assaying of the accumulation of radiophosphate in the dissolved pool (syringe filtration, 25 mm diameter polysulphone $0.2 \text{ }\mu\text{m}$ pore size filters, Cameo) started approximately one hour after addition of the competitive inhibitor and continued for 4 to 6 hours (Fig. 5.3.1a, step 9). The slope resulting from the accumulation of dissolved radiophosphate over time provided an estimate of the rate of release of dissolved P which was used to calculate the rate of dissolved P regeneration by plankton (Hudson & Taylor 1996; Hudson & Taylor 2005). The turnover rate of the particulate P pool (i.e., plankton) was calculated from the regeneration rate ($\text{ng l}^{-1} \text{ d}^{-1}$) divided by the particulate P concentration (ng l^{-1}). The steady

state PO_4^{3-} concentration (ssPO_4^{3-}) was also calculated: $\text{ssPO}_4^{3-} = R \text{ (pM min}^{-1}) \div k \text{ (min}^{-1})$, where R is the measured regeneration rate and k is the uptake constant (Hudson et al. 2000). In summary, we measured the effect of treatment on the turnover time of dissolved PO_4^{3-} , the regeneration rate of dissolved P, the turnover rate of particulate or planktonic P, and finally, on the concentration of ssPO_4^{3-} .

Effects of UVR on P Regeneration – Minimizing Recovery Time

An effect of UVR on the regeneration of dissolved P by plankton may be undetectable 4–12 h after incubation if plankton are capable of repairing rapidly (i.e., regeneration rates may need to be measured immediately after treatment or during treatment to detect an effect of UVR). Therefore, we performed two additional sets of experiments. Lakes for this sub-set of experiments were randomly selected to encompass a broad range in TP. Regeneration rates increase with increasing TP concentration (Hudson et al. 1999.). Therefore, it was assumed that encompassing a broad range in regeneration rates would increase our ability to determine if and when regeneration rates may be affected by UVR. Lake water (250 ml) was gently transferred into pre-washed polypropylene containers (Starfrit®, 350 ml), and carrier-free radiophosphate ($^{33}\text{PO}_4$, ICN Biomedicals, final activity $\sim 50\,000 \text{ cpm ml}^{-1}$) was injected (Fig. 5.3.1b, steps 2 and 3). Vessels were incubated in the dark (i.e., no exposure to sunlight) at ambient lake temperature for $\sim 12 \text{ h}$ to label the plankton assemblage prior to treatment. Three treatments (replicates, $n = 3$) were established as described above (Fig. 5.3.1b, step 4). In the first set of experiments water samples were incubated outdoors (between 9:00–16:00 h) in sunlight for $\sim 6 \text{ h}$ in a water bath (at ambient lake temperature) (Fig. 5.3.1b, step 4). Then these incubations were terminated with the addition of unlabelled $^{31}\text{PO}_4^{3-}$ as a competitive inhibitor (final

concentration 1 mg l^{-1}) (Hudson & Taylor 1996) and the regeneration of dissolved P and the turnover rate of particulate P were measured as already described (Fig. 5.3.1b, steps 5– 7). A second set of experiments was conducted with samples from an additional 2 lakes (Delaronde and Cowan Lakes). Experimental procedure followed the outline of Fig. 5.3.1b with the following modifications. Samples were incubated under artificial UVR (SunTest Solar Simulator, at 250 W m^{-2}) for 4h following the addition of competitive inhibitor so regeneration rates could be measured under constant UVR exposure.

Water Chemistry

DOC concentration was measured on a Shimadzu total organic carbon analyzer (TOC-5050A). Analysis for total and dissolved P was measured according to Parsons et al. (1984). The quantity of P in the particulate fraction ($>0.2 \text{ }\mu\text{m}$) was determined by subtracting dissolved P from total P. Chlorophyll *a* samples were collected on 47 mm GF/F (vacuum filtration 10 psi, under low light conditions). Chlorophyll pigments were extracted and analyzed according to Bergmann and Peters (1980) with the following changes; absorbance was read at 665nm rather than 655nm, and chl *a* samples were left in 95% ethanol for 24 h at room temperature rather than refrigerated (Arvola 1981; Dessouki et al. 2005). Chlorophyll samples were not corrected for phaeophytin.

Statistical Analysis

Treatment effects on the turnover time of the dissolved PO_4^{3-} pool, the regeneration of dissolved PO_4^{3-} , the turnover time of particulate P, ssPO_4^{3-} concentrations, and APA were determined with one-way analysis of variance (one-way ANOVA). Dunnet pairwise comparisons with a control (shade treatment) were performed when significant differences ($p < 0.05$) between treatments were observed. Differences in rates of

dissolved P regeneration and turnover rates of particulate P between treatments labeled with $^{33}\text{PO}_4^{3-}$ post-treatment (Fig. 5.3.1a) and pre-treatment (Fig. 5.3.1b) were also determined (one-way ANOVA). A relationship between the magnitude of decline in APA and PO_4^{3-} demand [i.e., the uptake constant (k)] in PAR+UVR treatments relative to the controls were analyzed with Pearson's correlation analysis. Treatments were deemed statistically significant at an alpha level of 0.05. Statistical analyses were performed with Statistica v. 6.1 (StatSoft, Inc., Tulsa, Oklahoma).

5.3.3. Results

Total P concentrations had a range of 5.9–102.7 $\mu\text{g l}^{-1}$, steady state PO_4^{3-} concentrations had a range of 0.35–42.5 ng l^{-1} , chl *a* concentrations had a range of 1.1–19.5 $\mu\text{g l}^{-1}$, and DOC concentrations had a range of 4.5–36.3 mg l^{-1} (Table 5.3.1). Total PAR radiation received by experimental trials had a range of 632 to 4195 (2045 ± 870 , mean ± 1 S.D.) ($\text{KJ m}^{-2} \text{h}^{-1}$). Total UVR received by experimental trials had a range of 133 to 433 (255 ± 77 , mean ± 1 S.D.) ($\text{KJ m}^{-2} \text{h}^{-1}$) (Table 5.3.2).

Table 5.3.2. Total incident solar radiation received by each experimental trial. PAR and total UVR (KJ m^{-2}) was obtained from nearby meteorological field stations for the three Ontario Lakes (Muskoka, Plastic, and Brandy) during the 2007 experiments. Separate measurements of UVA and UVB were not available from the meteorological field stations for the 2007 data. All other solar radiation measurements ($\text{KJ m}^{-2} \text{h}^{-1}$) were taken with an Ocean Optics USB2000 radiometer. nd = no data available

Lake	Date (ddmmyy)	PAR	Total UVR	UVA	UVB
Muskoka	260707	1100	132.9	nd	nd
Emerald	120707	nd	nd	nd	nd
Memorial	140708	2719	266.5	256.2	10.3
Lac la Pêche	090708	1868	219.2	210.6	8.6
Constance	290808	2677	344.1	332.6	11.4
Brandy	310707	1323	169	nd	nd
Pinkney	120808	1022	185.9	176.0	9.9
Turtle	050808	1951	223.3	217.9	5.4
Iroquois	220708	632	181.5	169.1	12.4
Little Loon	050808	1951	223.3	1217.9	5.4
Upper Blackstrap	280708	1864	265.0	250.8	14.3
Lower Blackstrap	280708	2734	322.6	312.7	9.9
Torch	010808	2450	303.2	291.5	11.7
Pelletier	170708	2377	288.1	280.2	7.9
Murray	070808	4145	432.7	419.3	13.4
Wildlife Pond	230708	2045	254.8	260.4	10.4

Effects of UVR on P cycling

Turnover times of the dissolved PO_4^{3-} pool in PAR+UVR treatments were significantly greater than control treatments in 10 of the 15 study lakes ($p \leq 0.04$) (Fig. 5.3.2). The uptake of $^{33}\text{PO}_4^{3-}$ was undetectable in the PAR+UVR treatment for Lac la Peche (Fig. 5.3.2) despite the control treatment having a rapid turnover time. A PAR effect on the turnover time of the dissolved PO_4^{3-} pool was undetectable (i.e., the turnover time was not significantly different from the control), except for one lake (Lac la Peche, $p = 0.048$, $n = 3$) (Fig. 5.3.2) which had an increase in the turnover time of the dissolved PO_4^{3-} pool.

Rates of dissolved P regeneration in the PAR+UVR treatment were not significantly different from the control treatment, except for one lake (Lac la Peche, $p < 0.001$, $n = 3$) which had a reduced rate of regeneration (Fig. 5.3.3a). Regeneration rates were unaffected by PAR. The PAR+UVR treatment did not affect the turnover rate ($\% \text{ d}^{-1}$) of the particulate P pool except for one lake (Lac la Peche, $p < 0.001$, $n = 3$) (Fig. 5.3.3b), which had a turnover rate less than the control treatment. An effect of PAR on the turnover rate of particulate P was not detected. Steady state PO_4^{3-} concentration in the PAR+UVR treatments increased significantly compared to the control treatments in 8 of the study lakes ($p \leq 0.05$) (Fig. 5.3.3c). An effect of PAR on steady state PO_4^{3-} concentration was observed in Lac la Peche only.

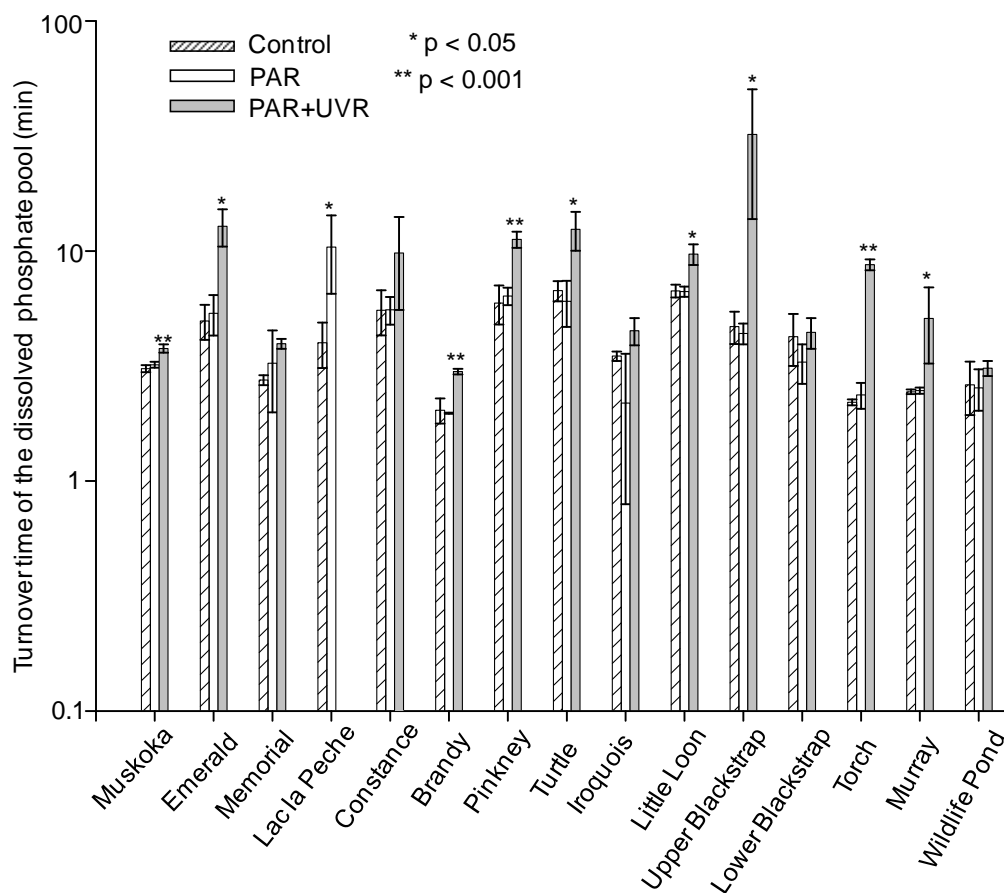


Figure 5.3.2. Turnover time of the dissolved phosphate pool (min \pm 1 S.D., $n = 3$) after lake water was exposed to experimental treatment (control, PAR, or PAR+UVR). Turnover times of the phosphate pool were greater in the PAR+UVR treatments compared to the control treatment. Note the uptake of $^{33}\text{PO}_4$ was undetectable in PAR+UVR treatment of Lac la Peche. An effect of PAR on the turnover time of the dissolved phosphate pool was undetectable except for one lake (Lac la Peche) where turnover times were greater than in the control treatment. Differences between treatments were determined with one-way ANOVA. Dunnet pairwise comparisons with a control were performed when significant differences ($p < 0.05$) between treatments were observed. * denotes values that are significantly different from the controls. Lakes increase in total P concentration from left to right.

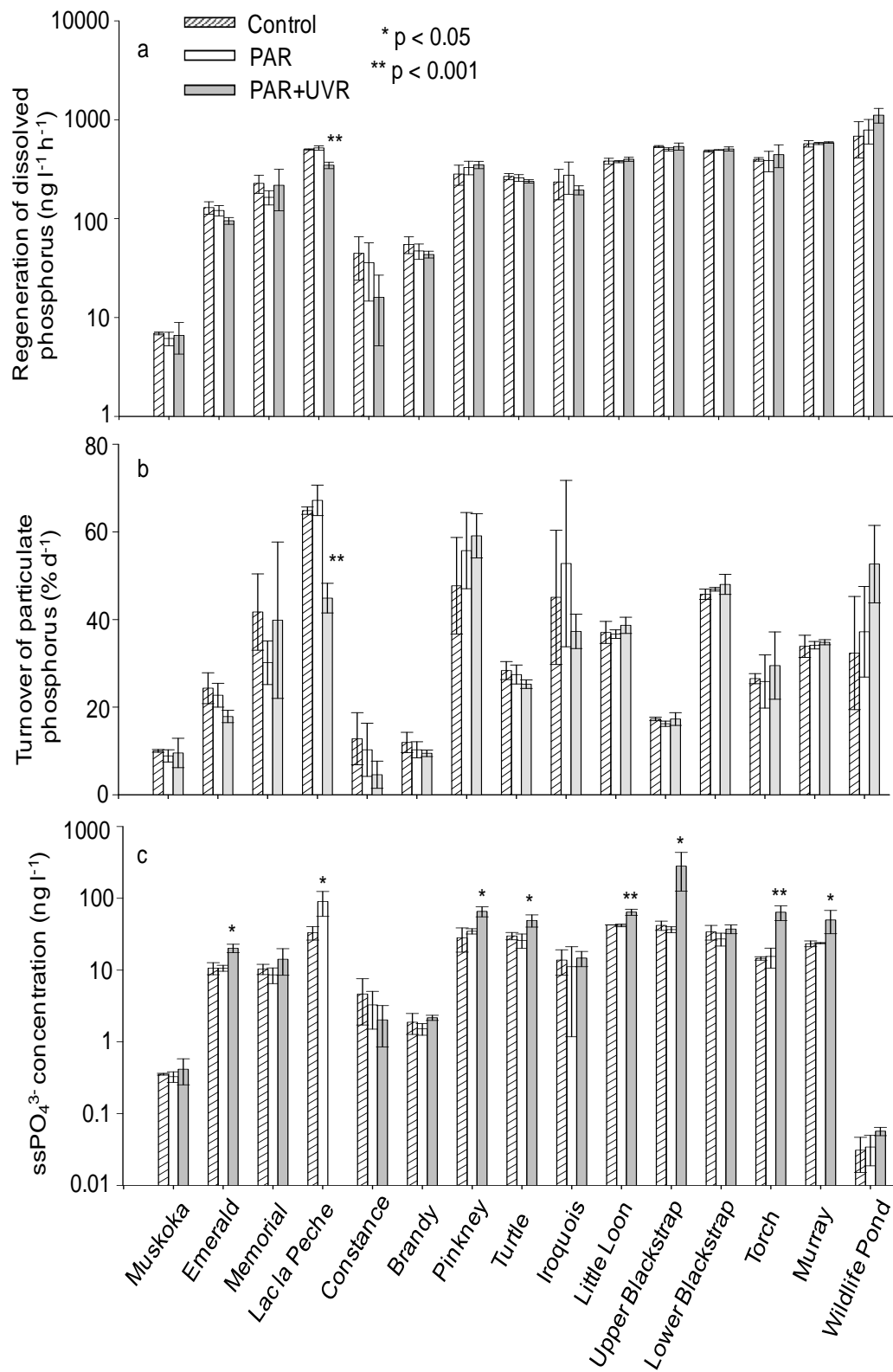


Figure 5.3.3. The effect of treatment on the regeneration of dissolved P (A), the turnover rate of particulate P (regeneration rate \div particulate P concentration) (B), and the steady state phosphate concentration [$\text{ssPO}_4 = \text{regeneration rate} \div k$ (uptake constant)] (C) (± 1 S.D., $n = 3$) for lake water that had been exposed to control, PAR, or PAR+UVR treatments. * denotes values that are significantly different from the controls. Lakes increase in total phosphorus concentration from left to right.

Effect of UVR on P regeneration: minimizing recovery time

We did not detect a significant treatment effect of UVR on dissolved P regeneration in our original set of experiments. We hypothesized that regeneration rates may need to be measured immediately following, or during UVR treatment to detect a treatment effect. Therefore, we performed an additional set of experiments with pre-labeled plankton assemblages.

The regeneration of dissolved P was unaffected by PAR and PAR+UVR treatments ($p \geq 0.06$), except for one lake, (Delaronde L.) (Fig. 5.3.4a). Likewise, the turnover rate of particulate P did not change under PAR+UVR treatment, except for 2 lakes, (Memorial L. and Delaronde, $p \leq 0.026$) (Fig. 5.3.4b). An effect of PAR treatment on the turnover rate of particulate P was not detected in any lake. Rates of dissolved P regeneration and the turnover rate of particulate P were not significantly different between treatments labeled with $^{33}\text{PO}_4^{3-}$ post-treatment (experiment A, Fig. 5.3.1) and pre-treatment (experiment B, Fig. 5.3.1) ($p \geq 0.11$) except for one lake, Memorial. Memorial L. had rates of dissolved P regeneration and turnover rates of particulate P in the PAR+UVR treatment that were significantly less (compare Figs. 5.3.3 and 5.3.4) in the pre-labeled experiment (experiment B, Fig. 5.3.1) than in post-labeled experiment (experiment A, Fig. 5.3.1) ($p = 0.01$).

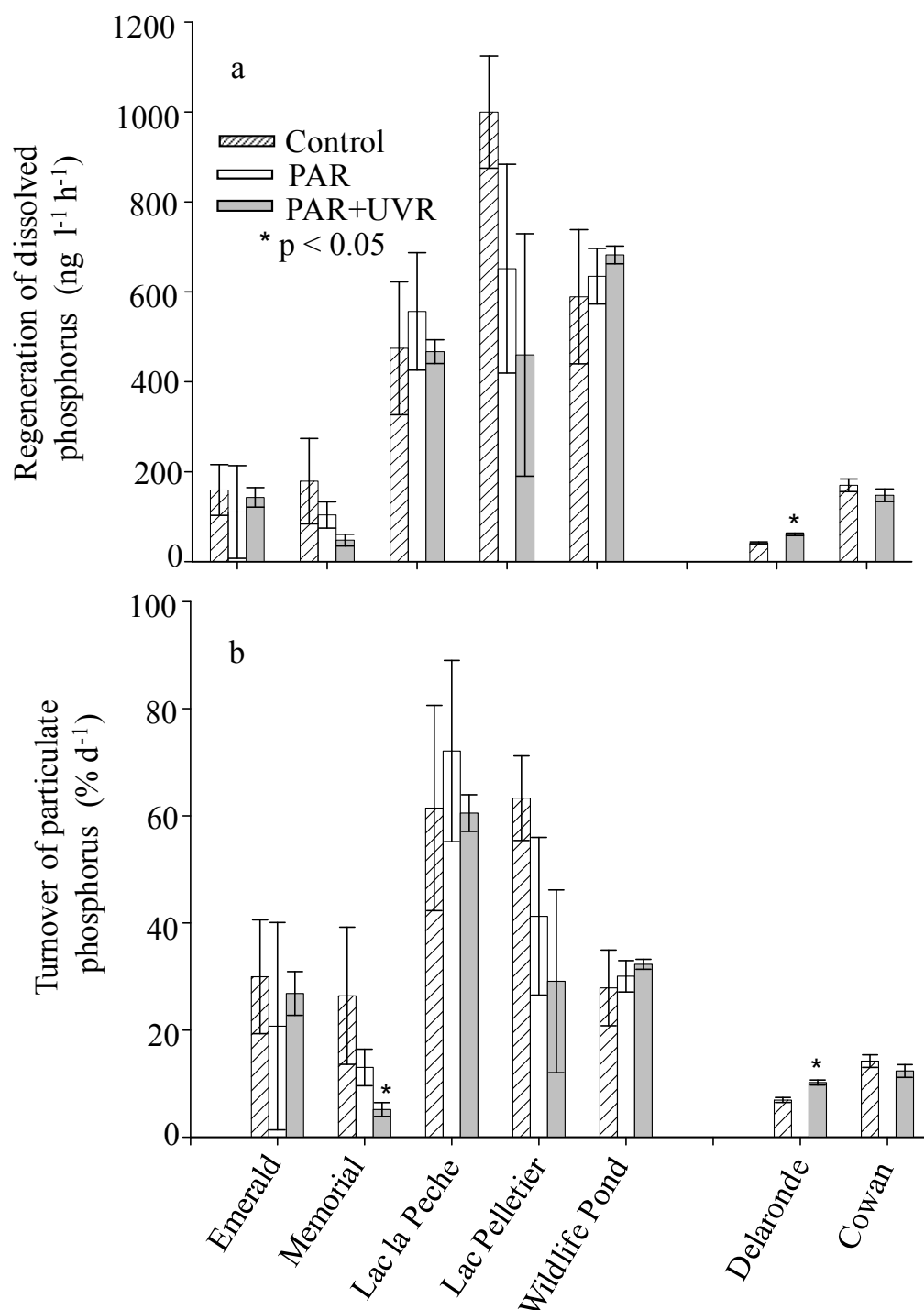


Figure 5.3.4. An effect of UVR on the regeneration of dissolved P by plankton may be undetectable 4–12 h after incubation if plankton are capable of repairing rapidly (i.e., regeneration rates may need to be measured immediately after or during treatment to detect an effect of UVR). Therefore, we performed an additional set of experiments with plankton assemblages that were pre-labeled (~12 h incubation with $^{33}\text{PO}_4^{3-}$) prior to

treatment. Shown are the effect of treatment on the regeneration of dissolved P (A), and the turnover of particulate P (regeneration rate \div particulate P concentration) (B) (± 1 S.D., $n = 3$) in lake water that had been exposed to experimental treatments (control, PAR, or PAR+UVR). Note regeneration rates for Delaronde and Cowan Lakes were measured under constant artificial UVR exposure (SunTest Solar Simulator, 250 W m^{-2}). * denotes values that are significantly different from the controls.

Effect of UVR on APA

Dissolved APA in the PAR+UVR treatment was less than in the control treatment (note dissolved APA was undetectable in Turtle Lake) ($p \leq 0.05$) (Fig. 5.3.5a). A treatment effect was not observed in 5 of the study lakes ($p > 0.05$). However, significantly greater phosphatase activity ($p = 0.02$) was observed in the PAR+UVR treatment of Lac Pelletier. An effect of the PAR treatment on dissolved APA was not detected ($p \geq 0.26$). Particulate APA activity in the PAR+UVR treatments was significantly lower than in the control treatments in 8 of the study lakes (Fig. 5.3.5b). An effect of the PAR treatment on particulate APA activity was not detected in any lake ($p \geq 0.06$). A relationship between the magnitude of decline in $^{33}\text{PO}_4^{3-}$ uptake (increase in turnover time) and the magnitude of decline in APA was not observed ($p \geq 0.29$, Pearson correlation analysis).

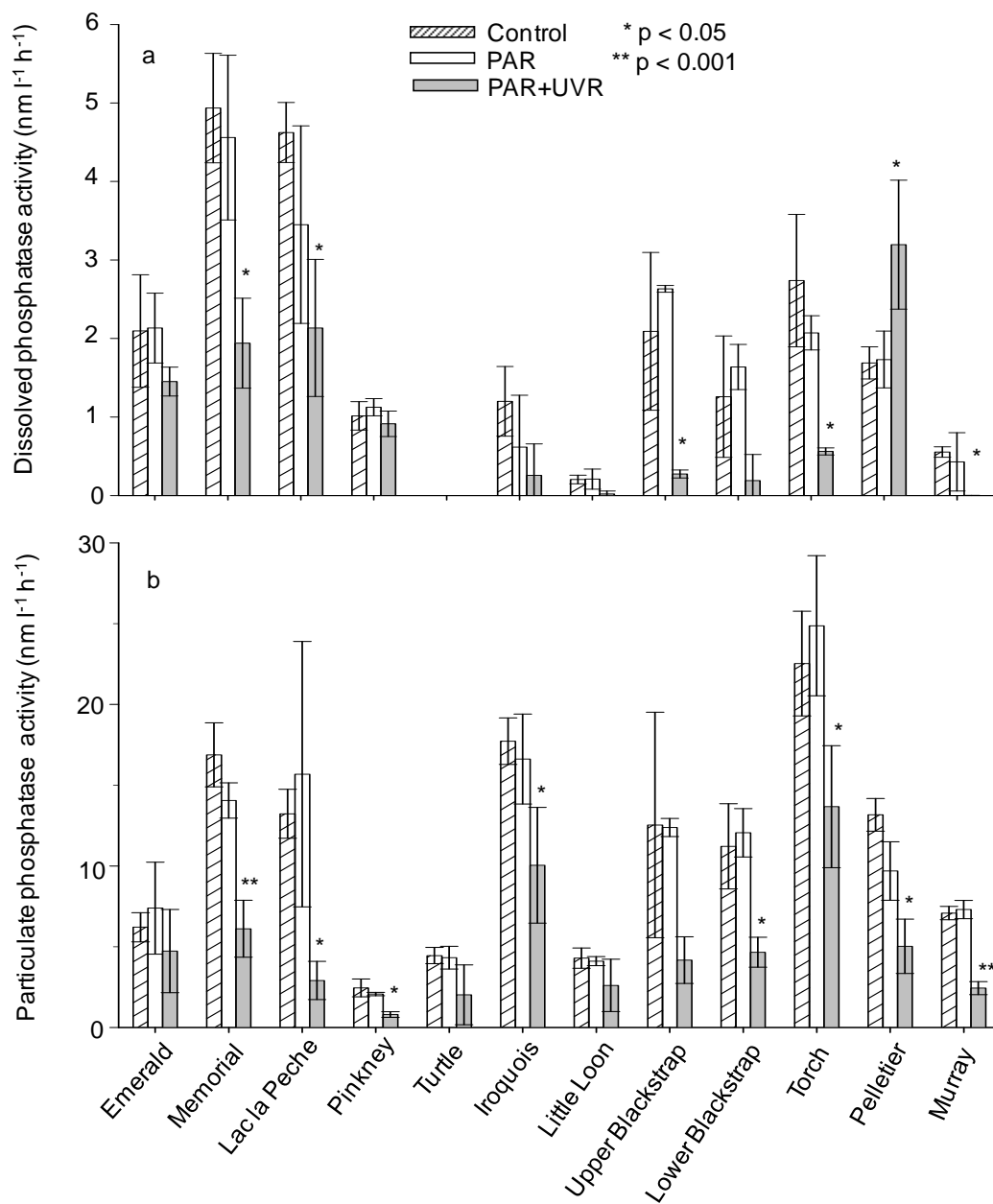


Figure 5.3.5. Alkaline phosphatase activity in the dissolved fraction ($<0.2 \mu\text{m}$) (A) and particulate fraction ($>0.2 \mu\text{m}$) (B) (± 1 S.D., $n = 3$) in lake water that was exposed to one of three experimental treatments; control, PAR, or PAR+UVR. * denotes values that are significantly different from the controls. Lakes increase in total phosphorus concentration from left to right.

5.3.4. Discussion

We provide the first direct evidence that the turnover time of the PO_4^{3-} pool significantly increases in natural plankton assemblages exposed to PAR+UVR at ambient PO_4^{3-} concentrations (Fig. 5.3.2). Our results are in contrast to past studies which have detected an effect of UVR at enhanced PO_4^{3-} concentrations only (Allen & Smith 2002; Frost & Xenopoulos 2002). The turnover time of the PO_4^{3-} pool is a measure of the demand to concentration ratio for PO_4^{3-} where rates of uptake and regeneration are tightly coupled (i.e., P-limited systems). Turnover times of the PO_4^{3-} pool in the control treatments of our study lakes were 2–7 min (Fig. 5.3.2) and are indicative of severe P-limitation (Lean & Nalewajko 1979). The observed increase in turnover time in the UVR treatments may reflect 1) an increased difficulty of plankton to acquire PO_4^{3-} as a result of damage to surface proteins required for P-uptake or, 2) a decrease in algal cellular demand for P if rates of algal growth and cell division declined under UVR exposure (Xenopoulos et al. 2002). Carbon(C):P ratios of phytoplankton have been shown to decline under UVR exposure (Xenopoulos et al. 2002; Carrillo et al. 2008; Hessen et al. 2008) which has led to the conclusion that P-uptake may be insensitive to UVR or at least less sensitive than rates of C-fixation (Frost & Xenopoulos 2002). However, declines in C:P ratios were detected under enhanced P concentrations (Frost & Xenopoulos 2002; Xenopoulos et al. 2002; Carrillo et al. 2008) and therefore, may be indicative of luxury P-uptake.

Under ambient lake conditions (i.e., ambient UVR irradiance and PO_4^{3-} concentrations) the uptake of P is frequently dominated by bacterioplankton (Currie & Kalf 1984; Currie et al. 1986) which are more sensitive to UVR exposure than larger

algae (Jeffrey et al. 1996; Hiriart et al. 2002). If either the ability of bacterioplankton to acquire PO_4^{3-} or the demand for PO_4^{3-} by bacteria is reduced, while larger algae are insensitive to UVR [i.e., because of internal self shading and the presence of photo-protective pigments) (Karentz et al. 1991; Garciapichel 1994)], then the large increase in turnover time of the PO_4^{3-} pool we observed is likely purely a bacterial response to UVR. Bacterioplankton were not captured on the glass fiber filters used in previous studies (Frost & Xenopoulos 2002; Xenopoulos et al. 2002; Aubriot et al. 2004) and likely explains the inability of previous studies to detect a UVR response in P-uptake. To our knowledge only one study has examined the effect of UVR on the size distribution of P-uptake and turnover (Allen & Smith 2002). Although, Allen and Smith (2002) did not detect an effect of cell size on P-uptake under UVR irradiance, their study was restricted to a single system (Lake Erie). Environmental moderating factors such as water clarity, mixing depth and rates (Neale et al. 1998), light history (Villafane et al. 1995; Helbling et al. 1999) and/or nutrition status (Lesser et al. 1994; Aubriot et al. 2004; Shelly et al. 2005) may have negated the ability of Allen and Smith to detect a treatment effect.

We were unable to detect a significant change in the regeneration of dissolved P except for 2 lakes, Lac la Peche, and Delaronde (Figs. 5.3.3a and 5.3.4a). The decrease in regeneration rate observed in Lac la Peche may be reflective of the retention of P for the repair of DNA, cellular membranes and/or proteins following UVR damage, as regeneration rates were measured post UVR exposure. In contrast, regeneration rates increased when measured under constant UVR exposure (Delaronde L., Fig. 5.3.4a). This probably reflects cellular P leakage as a result of cell membrane damage. However, the sensitivity of plankton to UVR is known to vary interspecifically and with organism size

(Leech & Williamson 2000; Sommaruga & Buma 2000). The sensitivity of planktonic P regeneration to UVR in the remainder of lakes may have been masked by the coarse resolution of our analysis. That is, changes in P regeneration by different size plankton would be undetectable when measuring P regeneration of the entire plankton assemblage. The retention of P for the repair of DNA, proteins and consequently RNA, and/or UVR induced reductions in grazing (Sommaruga et al. 1996) should result in reduced rates of dissolved P regeneration, particularly in UVR sensitive taxa. It is unclear if either the species composition or the size distribution of the plankton assemblage in either Lac la Peche or Memorial Lakes were such that they were more sensitive to UVR than the other study lakes. However, we do not believe that these measurements are erroneous. Nonetheless, the effect of UVR on the size specific rate of dissolved P regeneration remains unknown and further investigation is warranted.

We observed a significant increase in ssPO_4^{3-} concentration in UVR samples (Fig. 5.3.3c). The increase in ssPO_4^{3-} concentration is a result of a reduction in the uptake constant (k) (Fig. 5.3.2) without a change in the dissolved P regeneration (Fig. 5.3.3a) (i.e., $\text{ssPO}_4^{3-} = \text{regeneration rate} \div k$). The decrease in k may reflect an increased difficulty of plankton to acquire PO_4^{3-} as a result of damage to surface proteins required for P-uptake or, a decrease in algal P-demand because of reduced rates of algal growth and cell division. Regenerative processes are dominated by pico- and nanoplankton (Hudson & Taylor 1996; Nowlin et al. 2007); whereas, bacteria and algae account for the uptake of P (Currie et al. 1986; Currie & Kalf 1984). It is expected that the decline in P-demand may not be uniform as the sensitivity to UVR varies inter-specifically (Karentz et al. 1991; Arrieta et al. 2000) and with cell size (Karentz et al. 1991; Milot-Roy & Vincent

1994; Hiriart et al. 2002). The accumulation of PO_4^{3-} in the dissolved pool will create small-scale patches of elevated PO_4^{3-} concentration and may afford luxury uptake for plankton species and/or size fractions that are less sensitive to UVR. Moreover, increases in PO_4^{3-} demand for the recovery and repair of cellular membranes and proteins following UVR induced damage (Pausz & Herndl 2002; Hessen et al. 2008) could be satisfied by the observed increase in ssPO_4^{3-} concentration. However, this increase in uptake would be at the expense of species and/or size fractions that exhibit greater UVR sensitivity. Species that are more sensitive to UVR, in turn should experience reduced fitness, survival and reproduction rates. Competition for the acquisition and retention of PO_4^{3-} in limnetic systems exposed to high levels of UVR may therefore be a driving force structuring plankton assemblages to UVR tolerant taxa, larger potentially more UVR resistant cells, or the evolution of P-uptake systems that are insensitive to UVR.

Phosphatase activity generally declined under UVR exposure (Fig. 5.3.5). However, significantly greater dissolved phosphatase activity was observed in the PAR+UVR treatment of Lac Pelletier (Fig. 5.3.5a). DOC may bind to and inactivate dissolved phosphatases (Boavida & Wetzel 1980; Tank et al. 2005). However, phosphatase activity may be restored following the photodegradation of DOC and the release of organically bound phosphatases (Boavida & Wetzel 1980; Tank et al. 2005). Reactivation of organically bound phosphatases may explain the observed increases in APA in Lac Pelletier. It has been suggested that decreases in PO_4^{3-} uptake by planktonic assemblages exposed to UVR could be partly explained by a decline in labile P as a result of reduced APA (Tank et al. 2005). However, a relationship between the magnitude of decline in P-uptake (increase in turnover time) and the magnitude of decline in APA was not

observed. Therefore, the uptake rate of PO_4^{3-} in PAR+UVR exposed samples is not influenced by changes in APA, at least not over short time intervals that uptake rates are measured.

The observed decline in APA is assumed to be a result of photo-inactivation, as observed in past studies (Garde & Gustavson 1999; Tank et al. 2005). However, alkaline phosphatase synthesis is repressed by elevated PO_4^{3-} concentrations and the enzymes themselves are inhibited by high PO_4^{3-} concentrations (Jansson et al. 1988). It is conceivable that the observed increase in ssPO_4^{3-} (Fig. 5.3.3c) may have contributed to the reduction in APA; however, we did not directly test this hypothesis.

Conclusion

Our study is the first to demonstrate that UVR exposure has the potential to alter P cycling at ambient (picomolar) PO_4^{3-} concentrations. Despite significant declines in APA, the net effect of UVR exposure was an increase in the size of the dissolved PO_4^{3-} pool (ssPO_4^{3-}). In spite of prolonged periods of UVR exposure, the magnitude of treatment response was variable across lakes, and not all lakes responded to treatment. It is likely that multiple factors such as species composition (Karentz et al. 1991; Helbling et al. 1999), previous light exposure (Nalewajko et al. 1986; Villafane et al. 1995), nutritional status (Behrenfeld et al. 1994; Lesser et al. 1994; Aubriot et al. 2004; Heraud et al. 2005; Shelly et al. 2005), and cell size (Milot-Roy & Vincent 1994; Hiriart et al. 2002) interact in a complex manner to moderate plankton sensitivity to UVR that may not be revealed through simplistic lab or univariate field studies. While simplistic lab and univariate field studies offer some insight on the ecological effects of UVR, further investigation of the

interactive effects of multiple variables will be required to appreciably advance our ability to predict the effect of UVR on limnetic systems.

Chapter 6 – Synthesis and General Conclusions

6.1. Significance of Aquatic Metazoans

During summer the significance of external loading generally decreases and internal pathways (i.e. regeneration by aquatic metazoans, microorganisms and internal loading from the sediments) becomes increasingly significant in supplying nutrients to primary producers (Andersson et al. 1988). It has been demonstrated that the biomass of metazoans increases linearly along a trophic gradient in lakes (i.e. metazoan biomass increases with increasing total P) (Hanson & Leggett 1982; Hanson & Peters 1984; Wilson & Sarnelle 2002; Griffiths 2006). As such, total nutrient regeneration by aquatic metazoans also increases (Figs. 2.2, 3.2, 3.3). However, the magnitude and duration of internal loading from lake sediments, and the regeneration of dissolved P by microorganisms also increases with lake productivity (Bostrom et al. 1988; Hudson et al. 1999; Sondergaard 2001). In turn, the significance of aquatic metazoans in supplying nutrients for primary producers will depend on the magnitude of internal loading and the rate of dissolved P regeneration by microorganisms along a trophic gradient. The empirical models of metazoan nutrient release I have developed will complement empirical models for predicting internal loading from the sediments (Nürnberg 1984, 1988) and the regeneration of dissolved P by microorganisms (Hudson et al. 2005). Collectively, these models can be applied to limnetic systems and the significance of any single pathway may be determined both within and across systems. The ability to

integrate multiple internal pathways simultaneously represents a major advancement in limnology.

Internal loading from sediments may be a significant source of P supporting primary production during summer months, particularly for shallow lakes (Istvanovics et al. 2004). However, in deep lakes entrainment of P into the epilimnion will depend on water column stability (i.e. strength of the thermocline), and the concentration gradient between the hypolimnion and the epilimnion (Soranno et al. 1997). Therefore, the quantity of P actually entrained into the epilimnion may be low, despite accumulation of P in the hypolimnion (Soranno et al. 1997). This has led to the conclusion that benthic foraging fish may be important in nutrient cycling by crossing thermal barriers, and releasing nutrients into the epilimnion (i.e., benthic-pelagic coupling) (Schindler et al. 2001; Vander Zanden 2002). While the significance of detritivory versus non-detritivory on increasing total nutrient regeneration by fish has been clearly demonstrated (Fig 2.3), this pathway has rarely been placed into the context of the rates of nutrient release by other benthic foraging metazoans that undergo diel vertical migrations (e.g., *Gammarus*) (Aneer 1980; Madeira et al. 1982; Wilhelm et al. 1999). Benthic-pelagic coupling by macroinvertebrates represents a significant flux of nutrients particularly when invertebrate biomass is great (e.g. in fishless lakes) (Wilhelm et al. 1999). For example, rates of P regeneration by *Gammarus lacustis* in fishless Snowflake lake were ~5–17 times greater (Wilhelm et al. 1999) than rates of P regeneration by fish in a set of similar Alpine lakes (Schindler et al. 2001). Moreover, in the presence of fish, macroinvertebrate biomass and abundance declines. In turn, total nutrient excretion (all metazoans combined) decreases. This reflects the role of planktivorous fish in reducing the

abundance of macroinvertebrates which exhibit a greater mass specific excretion rate (Fig. 3.1).

The regeneration or recycling of nutrients from fish (through excretion or decomposition) has frequently been considered to be a significant source of P by comparing fish with a single and often trivial supply route such as allochthonous inputs (Kitchell et al. 1975; Schaus et al. 1997; Schindler et al. 2001). When placed into the context of other major supply routes (e.g., excretion by zooplankton or benthic macroinvertebrates) the release of nutrients by fish is generally minor. In the absence of mass mortality events (e.g., anadromous salmonides, Schindler et al. 2003), fish are a significant sink rather than source of nutrients in limnetic systems. This is reflected in the slow turnover of nutrients bound in fish biomass and through the loss of fish bound nutrients to the top of the food chain through a vertebrate loop (i.e., pg. 99) or lost from the system through scavenging by terrestrial vertebrates (Chidami & Amyot 2008). However, fish have rarely been examined in this context and further research on the fate of fish bones and their significance on the long term sequestering of P in lakes is required.

Our ability to quantify major internal pathways of P release has advanced with the development of my empirical models. What now remains unknown is an understanding of the significance of P release from littoral sediments (Andersen & Ring 1999; Cyr et al. 2009) and the contribution of macrophytes to P dynamics (Carignan & Kalf 1982; Granéli & Solander 1988) and further research is warranted. The models I have developed will now permit researchers to integrate these pathways into the P budget of lakes (i.e., compare P regeneration by aquatic metazoans with other major internal and

external pathways). Such an analysis will provide a comprehensive understanding of P cycling in lakes.

6.2. Effects of Ultraviolet Radiation on Phosphorus Kinetics

6.2.1. Abiotic Effects

A number of dissolved organic compounds are photodegradable to more biologically available forms that stimulate bacterial and primary production (Moran & Zepp, 1997). For example, >20% of the daily bacterial carbon demand and 30% of the daily nitrogen demand can be met through photodegradation of dissolved organic matter (DOM) in surface seawater (Moran & Zepp, 1997). Therefore, it was expected that the photodecomposition of DOP may be a significant source of PO_4^{3-} . However, the release of PO_4^{3-} was not immediately detectable in the majority of study lakes with our approach, despite a detectable breakdown of DOM through photochemical processes (Tables 5.1.4, 5.2.3). Nonetheless, the photochemical modification of DOM will increase its lability to microbial and enzymatic breakdown (e.g., APA) with PO_4^{3-} becoming available to plankton over a greater period of time (e.g. days to weeks). In turn, bacterial and algal growth would be stimulated, and phosphatase activity would decline in P-limited systems if the bioavailability of P increased following UVR irradiance. Consequently, biological (e.g. growth) and enzymatic (e.g. APA) assays may allow detection in slight changes in PO_4^{3-} availability in UVR exposed lake filtrates and further investigation is warranted.

In polymictic and shallow lakes substantial quantities of P laden sediments will reach the photic zone through wave turbulence. In these lakes, significant quantities of P should be released through photochemical processes (Fig. 5.2.1). The liberation of PO_4^{3-} from DOP was detectable in lake water with suspended sediments; however, limitations on our

ability to measure PO_4^{3-} concentrations chemically preclude the quantification of PO_4^{3-} released. Advances in the use of nuclear magnetic resonance (NMR) will allow for the quantification of PO_4^{3-} released from suspended sediments. NMR has not been applied to UVR studies and future research is necessary.

6.2.2. Biotic Effects

Ultraviolet radiation (UVR) also influences nutrient cycling biotically through changes in planktonic nutrient acquisition and release (Hessen et al. 1995; Allen & Smith 2002; Aubriot et al. 2004). I've presented the first comprehensive study to date on the biotic effects of UVR on P cycling at ambient (i.e., picomolar) PO_4^{3-} concentrations. Although the turnover time of the PO_4^{3-} pool increased, rates of dissolved P regeneration and the turnover rate of particulate P were only minimally affected by UVR exposure. Therefore, I concluded that the net effect of UVR was an increase in the size of the dissolved PO_4^{3-} pool (ss PO_4^{3-}) caused by a reduction in P uptake with unaltered rates of dissolved P regeneration. This increase in ss PO_4^{3-} is transient and disappears in a matter of hours once cells are shielded from UVR (Sereda et al. in review). Hence, the significance of this increase in ss PO_4^{3-} to primary producers is insignificant.

6.2. Summary

The empirical models I have developed are an important addition to other empirical models in the literature (e.g., Equations 1–4; Nürnberg 1998; Hudson et al. 2005) and contribute to the integration of aquatic metazoans into lake nutrient budgets. For the first time researchers will be able to examine inter- and intra-taxonomic variation in the rate of N and P release and its consequences for nutrient limitation within and across ecosystems (i.e., ecological stoichiometry effects). Although the photodecomposition of DOP does

not appear to be a significant pathway of PO_4^{3-} , additional research utilizing novel techniques such as NMR is warranted.

Finally, the relative importance of these different sources of P along trophic gradients across lakes is unknown. Future research should focus on placing these new understandings into context of other sources of P entering water bodies (e.g., from inlets, lake sediments and the atmosphere). Such analysis would represent a major advance in our understanding of the P cycle in limnetic systems.

Literature Cited

- Aldridge, D.W., Payne, B.S. & Miller, A.C. (1995) Oxygen consumption, nitrogenous excretion, and filtration rates of *Dreissena polymorpha* at acclimation temperatures between 20 and 32 degree C. *Canadian Journal of Fisheries and Aquatic Sciences*. **52**: 1761-1767.
- Allen, C. D., & Smith, R. E. H. (2002) The response of planktonic phosphate uptake and turnover to ultraviolet radiation in Lake Erie. *Canadian Journal of Fisheries and Aquatic Sciences*. **59**: 778-786.
- Alves, J.M., Caliman, A., Guariento, R.D., Figueiredo-Barros, M.P., Carneiro, L.S., Farjalla, V.F., Bozelli, R.L. & Esteves, F.A. (2010) Stoichiometry of benthic invertebrate nutrient recycling: interspecific variation and the role of body mass. *Aquatic Ecology*. **44**: 421-430.
- Andersen, F.Ø. & Ring, P. (1999) Comparison of phosphorus release from littoral and profundal sediments in a shallow, eutrophic lake. *Hydrobiologia*. **408**: 175-183.
- Anderson, R.S. (1972) Zooplankton composition and change in an alpine lake. *Verhandlung Internationale Vereinigung für Theoretische und Angewandte Limnologie*. **18**: 264-268.
- Anderson, R.S., & Donald D.B. (1978) Limnological survey of some small lakes in the vicinity of the Cascade Trail, Banff National Park. Miscellaneous report. Ottawa: Canadian Wildlife Service. 24p.
- Anderson, T.R. (1992) Modelling the influence of food C:N ratio, and respiration on growth and nitrogen excretion in marine zooplankton and bacteria. *Journal of Plankton Research*. **14**: 1645-1671.
- Andersson, G., Graneli, W., & Stenson, J. (1988) The Influence of Animals on Phosphorus Cycling in Lake Ecosystems. *Hydrobiologia*. **170**: 267-284.
- Andre, E.R., Hecky, R.E., & Duthie, H.C. (2003) Nitrogen and phosphorus regeneration by cichlids in the littoral zone of Lake Malawi, Africa. *Journal of Great Lakes Research*. **29**: 190-201.
- Arnott, D.L., & Vanni, M.J. (1996) Nitrogen and phosphorus cycling by the zebra mussel (*Dreissena polymorpha*) in the western basin of Lake Erie. *Canadian Journal of Fisheries and Aquatic Sciences*. **53**: 646-659.
- Arrieta J. M., Weinbauer, M. G. & Herndl, G. J. (2000) Interspecific variability in sensitivity to UV radiation and subsequent recovery in selected isolates of marine bacteria. *Applied & Environmental Microbiology*. **66**: 1468-1473.

- Arvola, L. (1981) Spectrophotometric determination of chlorophyll a and phaeopigments in ethanol extractions. *Annales Botanici Fennici*. **18**: 221-227.
- Atkinson, A. & Whitehouse, M.J. (2000) Ammonium excretion by Antarctic krill *Euphausia superba* at South Georgia. *Limnology and Oceanography*. **45**: 55-63.
- Atkinson, A. & Whitehouse, M.J. (2001) Ammonium regeneration by Antarctic mesozooplankton: an allometric approach. *Marine Biology*. **139**: 301-311.
- Attayde, J. L. & Hansson, L. A. (2001) The relative importance of fish predation and excretion effects on planktonic communities. *Limnology and Oceanography*. **46**: 1001-1012.
- Attayde, J. L. & Hansson, L. A. (1999) Effects of nutrient recycling by zooplankton and fish on phytoplankton communities. *Oecologia*. **121**: 47-54.
- Aubriot, L., Conde, D., Bonilla, S. & Sommaruga, R. (2004) Phosphate uptake behavior of natural phytoplankton during exposure to solar ultraviolet radiation in a shallow coastal lagoon. *Marine Biology*. **144**: 623-631.
- Bachmann R.W., Jones B.L., Fox D.D., Hoyer M., Bull L.A. & Canfield D.E. (1996) Relations between trophic state indicators and fish in Florida (USA) lakes. *Canadian Journal of Fisheries and Aquatic Sciences*. **53**: 842-855.
- Barlow, J.P. & Bishop, J.W. (1965) Phosphate regeneration by zooplankton in Cayuga Lake. *Limnology and Oceanography*. **10**: 15-24.
- Bartell, S.M. (1981) Potential impact of size-selective planktivory on phosphorus release by zooplankton. *Hydrobiologia*. **80**: 139-145.
- Bartell, S. M. & Kitchell, J. F. (1978) Seasonal impact of planktivory on phosphorus release by Lake Wingra zooplankton. *Verhandlungen der Internationalen Vereinigung fuer Theoretische und Angewandte Limnologie*. **20**: 466-474.
- Bayne, B.L. & Scullard, C. (1977) Rates of nitrogen-excretion by species of *Mytilus* (bivalvia-mollusca). *Journal of the Marine Biological Association of the United Kingdom*. **57**: 355-369
- Beamish, F.W.H. & Thomas, E. (1984) Effects of dietary-protein and lipid on nitrogen losses in rainbow-trout, *Salmo-gairdneri*. *Aquaculture*. **41**: 359-371.
- Behrenfeld, M. J., Lean, D. R. S. & Lee, H. (1995) Ultraviolet-B radiation effects on inorganic nitrogen uptake by natural plankton assemblages of oceanic plankton. *Journal of Phycology*. **31**: 25-36.

- Behrenfeld, M. J., Lee, H. & Small, L. F. (1994) Interactions between nutritional-status and long-term responses to ultraviolet-B radiation stress in a marine diatom. *Marine Biology*. **118**: 523-530.
- Benitez-Nelson, C. R. & Buesseler, K. O. (1999) Variability of inorganic and organic phosphorus turnover rates in the coastal ocean. *Nature*. **398**: 502-505.
- Bentzen, E. & Taylor, W. D. (1991) Estimating Michaelis-Menten parameters and lake water phosphate by the Rigler bioassay: Importance of fitting technique, plankton size and substrate range. *Canadian Journal of Fisheries and Aquatic Sciences*. **48**: 73-83.
- Bergman, E. (1990) Effects of roach, *Rutilus rutilus* on two percids, *Perca fluviatilis* and *Gymnocephalus cernus*: Importance of species interactions for diet shifts. *Oikos*. **57**: 241-249.
- Bergmann, M. & Peters, R. H. (1980) A simple reflectance method for the measurement of particulate pigment in lake water and its application to phosphorus-chlorophyll-seston relationships. *Journal of Fisheries and Aquatic Sciences*. **37**: 111-114.
- Biggs, D.C. (1982) Zooplankton excretion and NH₄⁺ cycling in near-surface waters of the southern-ocean. Ross Sea, Austral summer 1977-1978. *Polar Biology*. **1**: 55-67.
- Boavida, M. J. & Wetzel, R. G. (1998) Inhibition of phosphatase activity by dissolved humic substances and hydrolytic reactivation by natural ultraviolet light. *Freshwater Biology*. **40**: 85-293.
- Boers, P., Van Ballegooijen, L. & Uunk, J. (1991) Changes in phosphorus cycling in a shallow lake due to food web manipulations. *Freshwater Biology*. **25**: 9-20.
- Bostrom, B., Andersen, J. M., Fleischer, S. & Jansson, M. (1988) Exchange of phosphorus across the Sediment - Water Interface. *Hydrobiologia*. **170**: 229-244.
- Brabrand, A., Faafeng, B. A & Nilssen, J. P. M. (1990) Relative importance of phosphorus supply to phytoplankton production: fish excretion versus external loading. *Canadian Journal of Fisheries and Aquatic Sciences*. **47**: 364-372.
- Bray, R.N., Miller, A.C., Johnson, S., Krause, P.R., Robertson, D.L. & Westcott, A.M (1988) Ammonium excretion by macroinvertebrates and fishes on a subtidal rocky reef in southern California. *Marine Biology*. **100**: 21-30.
- Brooks, J. L. & Dodson, S. I. (1965) Predation, body size, and composition of plankton. *Science*. **150**: 28-35.

- Brown, J.H., Gillooly, F.G., Allen, A.P., Savage, V.M. & West, G.B. (2004) Toward a metabolic theory of ecology. *Ecology*. **85**: 117-1789.
- Brown, J.H., Allen, A.P., Gillooly, J.F., Hildrew, A., Raffaelli, D. & Edmonds-Brown, R. (2007) The metabolic theory of ecology and the role of body size in marine and freshwater ecosystems. *Body size: the structure and function of aquatic ecosystems. Ecological Reviews*. 1-15.
- Bunnell, D. B., Johnson, T. B. & Knight, C. T. (2005) The impact of introduced round gobies (*Neogobius melanostomus*) on phosphorus cycling in central Lake Erie. *Canadian Journal of Fisheries and Aquatic Sciences*. **62**: 15-29.
- Burnham, K.P., & Anderson, D. R. (2004) Multimodel inference - understanding AIC and BIC in model selection. *Sociological Methods and Research*. **33**: 261-304.
- Bushaw, K. L., Zepp, R. G., Tarr, M. A., Schulzjander, D., Bourbonniere, R. A., Hodson, R. E., Miller, W. L., Bronk, D. A. & Moran, M. A. (1996) Photochemical release of biologically available nitrogen from aquatic dissolved organic matter. *Nature*. **381**: 404-407.
- Canfield, D. E., Jones, J. R. & Bachmann, R. W. (1982) Sedimentary Losses of Phosphorus in Some Natural and Artificial Iowa Lakes. *Hydrobiologia*. **87**: 65-76.
- Carignan, R. & Kalf, J. (1982) Phosphorus release by submerged macrophytes: Significance to epiphyton and phytoplankton. *Limnology and Oceanography*. **27**: 419-427.
- Carignan, R., Planas, D. & Vis, C. (2000) Planktonic production and respiration in oligotrophic shield lakes. *Limnology and Oceanography*. **45**: 189-199.
- Carrillo P., Delgado-Molina, J. A., Medina-Sanchez, J. M., Bullejos, F. J. & Villar-Argaiz, M. (2008) Phosphorus inputs unmask negative effects of ultraviolet radiation on algae in a high mountain lake. *Global Change Biology*. **14**: 423-439.
- Cavender-Bares, K. K., Karl, D. M. & Chisholm, S. W. (2001) Nutrient gradients in the western North Atlantic Ocean: Relationship to microbial community structure and comparison to patterns in the Pacific Ocean. Deep-Sea Research I: *Oceanographic Research*. **48**: 2373-2395.
- Chidami, S. & Amyot, M. (2008) Fish decomposition in boreal lakes and biogeochemical implications. *Limnology and Oceanography*. **53**: 1988-1996.
- Cleveland, W.S. & Delvin, S.J. (1988). Locally weighted regression- an approach to regression-analysis by local fitting. *Journal of the American Statistical Association*. **83**: 596-610.

- Cockcroft, A.C. (1990) Nitrogen-excretion by the surf zone bivalves *Donax serra* and *Donax sordidus*. *Marine Ecology-Progress Series*. **60**: 57-65.
- Conroy, J.D., Edwards, W.J., Pontius, R.A., Kane, D.D., Zhang, H.Y., Shea, J.F., Richey, J.N. & Culver, D.A. (2005) Soluble nitrogen and phosphorus excretion of exotic freshwater mussels (*Dreissena* spp.): potential impacts for nutrient remineralisation in western Lake Erie. *Freshwater Biology*. **50**: 1146-1162.
- Cotner, J. B. & Heath, R. T. (1990) Iron redox effects on photosensitive phosphorus release from dissolved humic materials. *Limnology and Oceanography*. **35**: 1175-1181.
- Cotner, J.B. & Wetzel, R.G. (1992) Uptake of dissolved inorganic and organic phosphorus compounds by phytoplankton and bacterioplankton. *Limnology and Oceanography*. **37**: 232-243.
- Currie, D. J., Bentzen, E. & Kalff, J. (1986) Does algal-bacterial phosphorus partitioning vary among lakes? A comparative study of orthophosphate uptake and alkaline phosphatase activity in freshwater. *Canadian Journal of Fisheries and Aquatic Sciences*. **43**: 311-318.
- Currie, D. J. & Kalff, J. (1984) A comparison of the abilities of freshwater algae and bacteria to acquire and retain phosphorus. *Limnology and Oceanography*. **29**: 298-310.
- Cyr, H., McCabe, S.K. & Nürnberg, G.K. (2009) Phosphorus sorption experiments and the portential for interal phosphorus loading in littoral areas of a stratified lake. *Water Research*. **43**: 1654-1666.
- Degobbis, D. (1973) On the storage of seawater samples for ammonia determination. *Limnology and Oceanography*. **18**:146-150.
- Demers, E., McQueen, D. J., Popiel, S. A., Rocchi, A. M., Ramcharan, C. W. & Perezfuentetaja, A. (2001a) Changes in fish community structure. *Archiv für Hydrobiologie, Special Issues Advances in Limnology*. **56**: 23-48.
- Demers, E., McQueen, D.J., Ramcharan, C.W. & Perez-Fuentetaja, A. (2001b) Did piscivores regulate changes in fish commmunity structure? *Archiv für Hydrobiologie, Special Issues Advances in Limnology*. **56**: 49-80.
- Dessouki, T. C. E., Hudson, J. J., Neal, B. R. & Bogard, M. J. (2005) The effects of phosphorus additions on the sedimentation of contaminants in a uranium mine pit-lake. *Water Research*. **39**: 3055-3061.
- Dillon, P. J. & LaZerte, B. D. (1992) Response of the Plastic Lake catchment, Ontario, to reduced sulphur deposition. *Environmental Pollution*. **77**: 211-217.

- Dillon, P. J., McQueen, D. J., Ramcharan, C. W., Yan, N. D., Demers, E. & Hudson, J. J. (2001) Changes in nutrient and ion chemistry. *Archiv für Hydrobiologie Special Issues Advances in Limnology*. **56**: 227-255.
- Dillon, P. J. & Molot, L. A. (1997) Dissolved organic and inorganic carbon mass balance in Central Ontario lakes. *Biogeochemistry*. **36**: 29-42.
- Dillon, P. J., Reid, R. A. & Evans, H. E. (1993) The relative magnitude of phosphorus sources for small, oligotrophic lakes in Ontario, Canada. *Verhandlungen der Internationalen Vereinigung fuer Theoretische und Angewandte Limnologie*. **25**: 355-358.
- Dillon, P. J., & Rigler, F. H. (1974) Test of a Simple Nutrient Budget Model Predicting Phosphorus Concentration in Lake Water. *Journal of the Fisheries Research Board of Canada*. **31**:1771-1778.
- Dodds, W. K., Priscu, J. C. & Ellis, B. K. (1991) Seasonal uptake and regeneration of inorganic nitrogen and phosphorus in a large oligotrophic lake: size-fractionation and antibiotic treatment. *Journal of Plankton Research*. **13**: 1339-1358.
- Dohler, G. & Biermann, I. (1987) Effect of UV-B irradiance on the response of N-15-uptake of *Lauderia-annulata* and *Synedra-planctonica*. *Journal of Plankton Research*. **9**: 881-890.
- Durbin, E.G. & Durbin, A.G. (1981) Assimilation efficiency and nitrogen-excretion of a filter-feeding planktivore, the Atlantic Menhaden, *Brevoortia tyrannus* (Pisces, Clupeidae). *Fishery Bulletin*. **79**: 601-616.
- Ejsmont-Karabin, J. (1984) Phosphorus and nitrogen excretion by lake zooplankton (rotifers and crustaceans) in relationship to individual body weights of the animals, ambient temperature and presence or absence of food. *Ekologia Polsk*. **32**: 3-42.
- Elser, J.J. & Urabe, J. (1999) The stoichiometry of consumer-driven nutrient recycling: theory, observations, and consequences. *Ecology*. **80**: 735-751.
- Emmenegger, L., D., King, W., Sigg, L. & Sulzberger, B. (1998) Oxidation kinetics of Fe(III) in a eutrophic swiss lake. *Environmental Science and Technology*. **32**: 2990-2996.
- Emmenegger, L., Schonenberger, R. R., Sigg, L. & Sulzberger, B. (2001) Light-induced redox cycling of iron in circumneutral lakes. *Limnology and Oceanography*. **46**: 49-61.
- Flaten, G. A. F., Skjoldal, E. F., Krom, M. D., Law, C. S., Mantoura, R. F. C., Pitta, P., Psarra, S., Tanaka, T., Tselepidis, A., Woodward, E. M. S., Zohary, T. &

- Thingstad, T. F. (2005) Studies of the microbial P-cycle during a Lagrangian phosphate-addition experiment in the Eastern Mediterranean. *Deep-Sea Research Part II-Topical Studies in Oceanography*. **52**: 2928-2943.
- Flecker, A.S. (1996) Ecosystem engineering by a dominant detritivore in a diverse tropical stream. *Ecology*. **77**: 1845-1854.
- Francko, D. A., (1986) Epilimnetic phosphorus cycling: Influence of humic materials and iron on coexisting major mechanisms. *Canadian Journal of Fisheries and Aquatic Sciences*. **43**: 302-310.
- Francko, D. A. & Heath, R. T. (1979) Functionally distinct classes of complex phosphorus compounds in lake water. *Limnology and Oceanography*. **24**: 463-473.
- Francko, D. A. & Heath, R. T. (1982) UV-sensitive complex phosphorus: Association with dissolved humic material and iron in a bog lake. *Limnology and Oceanography*. **27**: 564-569.
- Fraser, J. M. (1981) Estimates of the standing stocks of fishes in four small Precambrian shield lakes. *Canadian Field-Naturalist*. **95**: 137-143.
- Forsberg, J.A. & Summerfelt, R.C. (1992) Effect of temperature on diel ammonia excretion of fingerling walleye. *Aquaculture*. **102**: 115-126.
- Frost, P. C. & Xenopoulos, M. A. (2002) Ambient solar ultraviolet radiation and its effects on phosphorus flux into boreal lake phytoplankton communities. *Canadian Journal of Fisheries and Aquatic Sciences*. **59**: 1090-1095.
- Fukuhara, H., & Sakamoto, M. (1988) Ecological significance of bioturbation of zoobenthos community in nitrogen release from bottom sediments in a shallow eutrophic lake. *Archiv Fur Hydrobiologie*. **113**: 425-445.
- Fukuhara, H., & Yasuda, K. (1989) Ammonium excretion by some fresh-water zoobenthos from a eutrophic lake. *Hydrobiologia*. **173**: 1-8.
- Furgal, J. A. & Smith, R. E. H. (1997) Ultraviolet radiation and photosynthesis by Georgian Bay phytoplankton of varying nutrient and photoadaptive status. *Canadian Journal of Fisheries and Aquatic Sciences*. **54**: 1659-1667.
- Garber, K. J., & Hartman, R. T. (1985) Internal phosphorus loading to shallow Edinboro Lake in Northwestern Pennsylvania. *Hydrobiologia*. **122**: 45-52.
- Garde, K. & Gustavson, K. (1999) The impact of UV-B radiation on alkaline phosphatase activity in phosphorus-depleted marine ecosystems. *Journal of Experimental Marine Biology and Ecology*. **238**: 93-105.

- Gardner, W.S., Nalepa, T.F., Quigley, M.A. & Malczyk, J.M. (1981) Release of phosphorus by certain benthic invertebrates. *Canadian Journal of Fisheries and Aquatic Sciences*. **38**: 978-981.
- Gennings, C., Molot, L. A. & Dillon, P. J. (2001) Enhanced photochemical loss of organic carbon in acidic waters. *Biogeochemistry*. **52**: 339-354.
- Gido, K.B. (2002) Interspecific comparisons and the potential importance of nutrient excretion by benthic fishes in a large reservoir. *Transactions of the American Fisheries Society*. **131**: 260-270.
- Gillooly, J.F., Brown, J.H., West, G.B., Savage, V.M. & Charnov, E.L. (2001) Effects of size and temperature on metabolic rate. *Science*. **293**: 2248-2251.
- Graham, M. D., Vinebrooke, R. D. & Turner, M. (2006) Coupling of boreal forests and lakes: Effects of conifer pollen on littoral communities. *Limnology and Oceanography*. **51**: 1524-1529.
- Granéli, W. & Solander, D. (1988) Influence of aquatic macrophytes on phosphorus cycling in lakes. *Hydrobiologia*. **1**: 245-266.
- Gray, J.S. (1985) Nitrogenous excretion by meiofauna from coral-reef sediments - Mecor-5. *Marine Biology*. **89**: 31-35.
- Griffiths, D. (2006) The direct contribution of fish to lake phosphorus cycles. *Ecology of Freshwater Fish*. **15**: 86-95.
- Grimm, N.B. (1988) Role of macroinvertebrates in nitrogen dynamics of a desert stream. *Ecology*. **69**: 1884-1893.
- Gulati, R.D., Ejsmont-karabin, J., Rooth, J. & Siewertsen, K. (1989) A laboratory study of phosphorus and nitrogen-excretion of *Euchlanis dilatata lucksiana*. *Hydrobiologia*. **186**: 347-354.
- Guy, M., Taylor, W. D. & Carter, J. C. H. (1994) Decline in total phosphorus in the surface waters of lakes during summer stratification, and its relationship to size distribution of particles and sedimentation. *Canadian Journal of Fisheries and Aquatic Sciences*. **51**: 1330-1337.
- Håkanson, L. (1995) Models to predict net and gross sedimentation in lakes. *Marine and Freshwater Research*. **46**: 305-319.
- Håkanson, L., Ostapenia, A. P. & Boulion, V. V. (2003) A mass-balance model for phosphorus in lakes accounting for bio-uptake and retention in biota. *Freshwater Biology*. **48**: 928-950.

- Hanson, J.M. & Leggett, W.C. (1982) Empirical prediction of fish biomass and yield. *Canadian Journal of Fisheries and Aquatic Sciences*. **39**: 257-263.
- Hanson, J.M. & Peters, R.H. (1984) Empirical prediction of crustacean zooplankton biomass and profundal macrobenthos biomass in lakes. *Canadian Journal of Fisheries and Aquatic Sciences*. **41**: 439-445.
- Hargrave, B.T. & Geen, G.H. (1968) Phosphorus excretion by zooplankton. *Limnology and Oceanography*. **13**: 332-342.
- Heath, R. T., (1986) Dissolved organic phosphorus-compounds - do they satisfy planktonic phosphate demand in summer. *Canadian Journal of Fisheries and Aquatic Sciences*. **43**: 343-350.
- Helbling, E. W., Villafane, V., Ferrario, M. & Holmhansen, O. (1992) Impact of natural ultraviolet radiation on rates of photosynthesis and on specific marine-pytoplankton species. *Marine Ecology-Progress Series*. **80**: 89-100.
- Henry, R. & Santos, C.M. (2008) The importance of excretion by Chironomus larvae on the internal loads of nitrogen and phosphorus in a small eutrophic urban reservoir. *Brazilian Journal of Biology*. **68**: 349-357.
- Heraud, P., Roberts, S., Shelly, K. & Beardall, J. (2005) Interactions between UV-B exposure and phosphorus nutrition. II. Effects on rates of damage and repair. *Journal of Phycology*. **41**: 1212-1218.
- Hernandez-Leon, S. & Ikeda, T. (2005) A global assessment of mesozooplankton respiration in the ocean. *Journal of Plankton Research*. **27**: 153-158.
- Hessen, D. O., Leu, E., Faerovig, P. J. & Petersen, S. F. (2008) Light and spectral properties as determinants of C:N:P-ratios in phytoplankton. *Deep-Sea Research Part II: Topical Studies in Oceanography*. **55**: 2169-2175.
- Hessen, D. O., Van-Donk, E. & Andersen, T. (1995) Growth responses, P-uptake and loss of flagellae in Chlamydomonas reinhardtii exposed to UV-B. *Journal of Plankton Research*. **17**: 17-27.
- Hewett, S.W. & Johnson, B.J. (1992) Fish bioenergetics model 2. University of Wisconsin Sea Grant Institute, Technical Report WIS-SG-92-250, Madison. Wisconsin
- Higgins, K.A., Vanni, M.J. & Gonzalez, M.J. (2006) Detritivory and the stoichiometry of nutrient cycling by a dominant fish species in lakes of varying productivity. *Oikos*. **114**: 419-430.

- Hirche, H.J. (1983) Excretion and Respiration of the Antarctic Krill *Euphausia superba*. *Polar Biology*. **1**: 205-209.
- Hiriart, V. P., Greenberg, B. M., Guildford, S. J. & Smith, R. E. H. (2002) Effects of ultraviolet radiation on rates and size distribution of primary production by Lake Erie phytoplankton. *Canadian Journal of Fisheries and Aquatic Sciences*. **59**: 317-328.
- Horppila, J. (1998) Effects of mass removal and variable recruitment on nutrient excretion by a planktivorous roach stock. *Journal of Fish Biology*. **52**: 951-961.
- Houser, J. N., Carpenter, S. R. & Cole, J. J. (2000) Food web structure and nutrient enrichment: effects on sediment phosphorus retention in whole-lake experiments. *Canadian Journal of Fisheries and Aquatic Sciences*. **57**: 1524-1533.
- Hudson, J. J., & Taylor, W. D. (1996) Measuring regeneration of dissolved phosphorus in planktonic communities. *Limnology and Oceanography*. **41**: 1560-1565.
- Hudson, J. J., & Taylor, W. D. (2005) Rapid estimation of phosphate at picomolar concentrations in freshwater lakes with potential application to P-limited marine systems. *Aquatic Sciences*. **67**: 316-325.
- Hudson, J. J., Taylor, W. D., McQueen, D. J. & Somers, K. M. (2001) Phosphorus in pelagic food webs. *Archiv für Hydrobiologie, Special Issues Advances in Limnology*. **56**: 211-225.
- Hudson, J. J., Taylor, W. D. & Schindler, D. W. (1999) Planktonic nutrient regeneration and cycling efficiency in temperate lakes. *Nature*. **400**: 659-661.
- Hudson, J. J., Taylor, W. D. & Schindler, D. W. (2000) Phosphate concentrations in lakes. *Nature*. **406**: 54-56.
- Ikeda, T. (1985) Metabolic rates of epipelagic marine zooplankton as a function of body-mass and temperature. *Marine Biology*. **85**: 1-11.
- Istvanovics, V., Osztóics, A. & Honti, M. (2004) Dynamics and ecological significance of daily internal load of phosphorus in shallow Lake Balaton, Hungary. *Freshwater Biology*. **49**: 232-252.
- James, M.R., Weatherhead, M.A. & Ross, A.H. (2001) Size-specific clearance, excretion, and respiration rates, and phytoplankton selectivity for the mussel *Perna canaliculus* at low levels of natural food. *New Zealand Journal of Marine and Freshwater Research*. **35**: 73-86.
- Jansson, M. (1979) Nutrient Budgets and the Regulation of Nutrient Concentrations in a Small Sub-Arctic Lake in Northern Sweden. *Freshwater Biology*. **9**: 213-231.

- Jansson, M., Olsson, H. & Pettersson, K. (1988) Phosphatases; origin, characteristics and function in lakes. *Hydrobiologia*. **170**:157-175.
- Jatteau, P. (1997) Daily patterns of ammonia nitrogen output of Siberian sturgeon *Acipenser baeri* (Brandt) of different body weights. *Aquaculture Research*. **28**: 551-557.
- Jawed, M. (1973) Ammonia excretion by zooplankton and its significance to primary productivity during summer. *Marine Biology*. **23**: 115-120.
- Jeffrey, W. H., Aas, P., Maille Lyons, M., Coffin, R. B., Pledger, R. J. & Mitchell, D. L. (1996) Ambient solar radiation-induced photodamage in marine bacterioplankton. *Photochemistry & Photobiology*. **64**: 419-427.
- Jeppesen, E., Jensen, J.P., Sondergaard, M., Lauridsen, T. & Landkildehus, F. (2000) Trophic structure, species richness and biodiversity in Danish lakes: changes along a phosphorus gradient. *Freshwater Biology*. **45**: 201-218.
- Jobling, M. (1981) Some effects of temperature, feeding and body-weight on nitrogenous excretion in young plaice *Pleuronectes platessa* L. *Journal of Fish Biology*. **18**: 87-96.
- Jordan, T.E. & Valiela, I. (1982) A nitrogen budget of the ribbed mussel, *Geukensia demissa*, and its significance in nitrogen flow in a New-England salt-marsh. *Limnology and Oceanography*. **27**: 75-90.
- Jayson, G. G., Swallow, A. J. & Parsons, B. J. (1972) Oxidation of ferrous ions by hydroxyl radicals. *Journal of the Chemical Society-Faraday Transactions I*. **68**: 2053-2058.
- Karentz, D., Cleaver, J. E. & Mitchell, D. L. (1991) Cell-survival characteristics and molecular responses of antarctic phytoplankton to ultraviolet-B radiation. *Journal of Phycology*. **27**: 326-341.
- Kelly, D. J., Bothwell, M. L. & Schindler, D. W. (2003) Effects of solar ultraviolet radiation on stream benthic communities: An intersite comparison. *Ecology*. **84**: 2724-2740.
- Kelso, J. R. M. (1985) Standing stock and production of fish in a cascading lake system on the Canadian shield. *Canadian Journal of Fisheries and Aquatic Sciences*. **42**: 1315-1320.
- Kelso J. R. M. & Johnson, M. G. (1991) Factors related to the biomass and production of fish communities in small, oligotrophic lakes vulnerable to acidification. *Canadian Journal of Fisheries and Aquatic Sciences*. **48**: 2523-2532.

- Kieber, R. J., Li, A. & Seaton, P. J. (1999) Production of nitrite from the photodegradation of dissolved organic matter in natural waters. *Environmental Science and Technology*. **33**: 993-998.
- Kieber, R. J., Zhou, X. & Mopper, K. (1990) Formation of carbonyl compounds from UV-induced photodegradation of humic substances in natural waters: Fate of riverine carbon in the sea. *Limnology and Oceanography*. **35**: 1503-1515.
- Kiibus, M. & Kautsky, N. (1996) Respiration, nutrient excretion and filtration rate of tropical freshwater mussels and their contribution to production and energy flow in Lake Kariba, Zimbabwe. *Hydrobiologia*. **331**: 25-32.
- Kilham, P. & Soltau-Kilham, S. (1990) Endless summer: Internal loading processes dominate nutrient cycling in tropical lakes. *Freshwater Biology*. **23**: 379-389.
- Kitchell, J. F., Koonce, J. F. & Tennis, P. S. (1975) Phosphorus flux through fishes. *Verhandlungen der Internationalen Vereinigung fuer Theoretische und Angewandte Limnologie*. **19**: 2478-2484.
- Koenings, J. P. & Hooper, F. F. (1976) The influence of colloidal organic matter on iron and iron-phosphorus cycling in an acid bog lake. *Limnology and Oceanography*. **21**: 684-696.
- Kopacek, J., Klementova, P. & Norton, S. A. (2005) Photochemical production of ionic and particulate aluminum and iron in lakes. *Environmental Science and Technology*. **39**: 3656-3662.
- Kraft, C.E. (1992) Estimates of phosphorus and nitrogen cycling by fish using a bioenergetics approach. *Canadian Journal of Fisheries and Aquatic Sciences*. **49**: 2596-2604.
- Kraft, C. E. (1993) Phosphorus regeneration by Lake Michigan alewives in the mid-1970s. *Transactions of the American Fisheries Society*. **122**: 749-755.
- Kremer, P., (1977) Respiration and excretion by ctenophore *Mnemiopsis leidyi*. *Marine Biology*. **44**: 43-50.
- Kremer, P., Canino, M.F. & Gilmer, R.W. (1986) Metabolism of epipelagic tropical ctenophores. *Marine Biology*. **90**: 403-412.
- Kuenzler, E.J. (1961) Phosphorus budget of a mussel population. *Limnology and Oceanography*. **6**: 400-415.
- Lamarra, V.A. (1975) Digestive activities of carp as a major contributor to the nutrient loading of lakes. *Verhandlungen der Internationalen Vereinigung fuer Theoretische und Angewandte Limnologie*. **19**: 2461-2468.

- Larocque, I., Mazumder, A., Proulx, M., Lean, D. R. S. & Pick, F. R. (1996) Sedimentation of algae: Relationships with biomass and size distribution. *Canadian Journal of Fisheries and Aquatic Sciences*. **53**: 1133-1142.
- Lean, D. R. S. (1984) Metabolic indicators for phosphorus limitation. *Verhandlungen der Internationalen Vereinigung fuer Theoretische und Angewandte Limnologie*. **22**: 211-218.
- Lean, D. & Nalewajko, C. (1979) Phosphorus turnover time and phosphorus demand in large and small lakes. *Archives fur Hydrobiologie Beih. Ergebnisse der Limnologie*. **13**: 120-132.
- Lean, D. & Pick, F. R. (1981) Photosynthetic response of lake plankton to nutrient enrichment: A test for nutrient limitation. *Limnology and Oceanography*. **26**: 1001-1019.
- Leech, D. M. & Williamson, C. E. (2000) Is tolerance to UV radiation in zooplankton related to body size, taxon, or lake transparency? *Ecological Applications*. **10**: 1530-1540.
- Lesser, M. P., Cullen, J. J. & Neale, P. J. (1994) Carbon uptake in a marine diatom during acute exposure to ultraviolet-B radiation – relative importance of damage and repair. *Journal of Phycology*. **30**: 183-192.
- Levine, S.N. & Schindler, D.W. (1999) Influence of nitrogen to phosphorus supply ratios and physicochemical conditions on cyanobacteria and phytoplankton species composition in the Experimental Lakes Area, Canada. *Canadian Journal of Fisheries and Aquatic Sciences*. **56**: 451-466.
- Locke, B. A. & E. de Grosbois (1986). Meteorological database for the Muskoka/Haliburton area. Ontario, Queen's Printer for Ontario.
- Lorenzen, K. (1996) The relationship between body weight and natural mortality in juvenile and adult fish: A comparison of natural ecosystems and aquaculture. *Journal of Fish Biology*. **49**: 627-647.
- Mack, J. & Bolton, J. R. (1999) Photochemistry of nitrite and nitrate in aqueous solution: A review. *Journal of Photochemistry and Photobiology a-Chemistry*. **128**: 1-13.
- Madeira, P.T., Brooks, A.S. & Seale, D.B. (1982) Excretion of total phosphorus, dissolved reactive phosphorus, ammonia, and urea by Lake-Michigan Mysis-Relicta. *Hydrobiologia*. **93**: 145-154.
- Maloney, K. O., Morris, D. P., Moses, C. O. & Osburn, C. L. (2005) The role of iron and dissolved organic carbon in the absorption of ultraviolet radiation in humic lake water. *Biogeochemistry*. **75**: 393-407.

- Martin, S., Thouzeau, G., Chauvaud, L., Jean, F., Guerin, L. & Clavier, J. (2006) Respiration, calcification, and excretion of the invasive slipper limpet, *Crepidula fornicata* L.: Implications for carbon, carbonate, and nitrogen fluxes in affected areas. *Limnology and Oceanography*. **51**: 1996-2007.
- Mather, M.E., Vanni, M.J., Wissing, T.E., Davis, S.A. & Schaus, M.H. (1995) Regeneration of nitrogen and phosphorus by bluegill and gizzard shad: effect of feeding history. *Canadian Journal of Fisheries and Aquatic Sciences*. **52**: 2327-2338.
- Mauzerall, D., Borowska, Z. & Zielinski, I. (1993) Photo and thermal-reactions of ferrous hydroxide. *Origins of Life and Evolution of the Biosphere*. **23**: 105-114.
- Mazumder, A., McQueen, D. J., Taylor, W. D. & Lean, D. R. S. (1988) Effects of fertilization and planktivorous fish (yellow perch) predation on size distribution of particulate phosphorus and assimilated phosphate: large enclosure experiments. *Limnology and Oceanography*. **33**: 421-430.
- McIntyre, P.B., Jones, L.E., Flecker, A.S. & Vanni, M.J. (2007) Fish extinctions alter nutrient recycling in tropical freshwaters. *Proceedings of the National Academy of Sciences of the United States of America*. **104**: 4461-4466.
- Mckaye, K.R. (1983) Ecology and breeding-behavior of a cichlid fish, *Cyrtocara eucinostomus*, on a large lek in Lake Malawi, Africa. *Environmental Biology of Fishes*. **8**: 81-96.
- McQueen, D. J., Ramcharan, C. W., Yan, N. D., Demers, E., Perez-Fuentetaja, A. & Dillon, P. J. (2001) Objectives, methods, the physical-chemical setting. *Archiv für Hydrobiologie Special Issues Advances in Limnology*. **56**: 1-21.
- Mehner, T., Ihlau, J., Dorner, H., Hupfer, M. & Holker, F. (2007) The role of insectivorous fish in fostering the allochthonous subsidy of lakes. *Limnology and Oceanography*. **52**: 2718-2721.
- Mehner, T., Mattukat, F., Bauer, D., Voigt, H. & Benndorf, J. (1998) Influence of diet shifts in underyearling fish on phosphorus recycling in a hypertrophic biomanipulated reservoir. *Freshwater Biology*. **40**: 759-769.
- Mellina, E., Rasmussen, J.B. & Mills, E.L. (1995) Impact of zebra mussel (*Dreissena polymorpha*) on phosphorus cycling and chlorophyll in lakes. *Canadian Journal of Fisheries and Aquatic Sciences*. **52**: 2553-2573.
- Meyer, J.L. & Schultz, E.T. (1985) Migrating haemulid fishes as a source of nutrients and organic-matter on coral reefs. *Limnology and Oceanography*. **30**: 146-156.

- Miller, W. L., King, D.W., Lin J. & Kester, D. R. (1995) Photochemical redox cycling of iron in coastal seawater. *Marine Chemistry*. **50**: 63-77.
- Mills, K. H., Chalanchuk, S. M. & Allen, D. J. (2002) Abundance, annual survival, and recruitment of unexploited and exploited lake charr, *Salvelinus namaycush*, populations at the Environmental Lakes Area, northwestern Ontario. *Environmental Biology of Fish*. **64**: 281-292.
- Milot-Roy V. & Vincent, W. F. (1994) UV radiation effects on photosynthesis: The importance of near-surface thermoclines in a subarctic lake. *Archives fur Hydrobiologie Beih. Ergebnisse der Limnologie*. **43**: 71-184.
- Molot, L.A., Hudson, J. J., Dillon, P. J. & Miller, S. A. (2005) Effect of pH on photo-oxidation of dissolved organic carbon by hydroxyl radicals in a coloured, softwater stream. *Aquatic Sciences*. **67**: 189-195.
- Monaghan, E. J. & Ruttenberg, K. C. (1999) Dissolved organic phosphorus in the coastal ocean: reassessment of available methods and seasonal phosphorus profiles from the Eel River Shelf. *Limnology and Oceanography*. **44**:1702-1714.
- Mopper, K., Zhou, X., Kieber, R. J., Kieber, D. J., Sikorski R. J. & Jones, R. D. (1991) Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle. *Nature*. **353**: 60-62.
- Morales-Baquero, R., Pulido-Villena, E. & Reche, I. (2006) Atmospheric inputs of phosphorus and nitrogen to the southwest Mediterranean region: Biogeochemical responses of high mountain lakes. *Limnology and Oceanography*. **51**: 830-837.
- Moran, M. A., & Zepp, R. G. (1997) Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnology and Oceanography*. **42**:1307-1316.
- Nakashima, B. S. & Leggett, W. C. (1980) The role of fish in the regulation of phosphorus availability in lakes. *Canadian Journal of Fisheries and Aquatic Sciences*. **37**: 1540-1549.
- Nalepa, T.F., Gardner, W.S. & Malczyk, J.M. (1991) Phosphorus cycling by mussels (Unionidae, Bivalvia) in Lake St-Clair. *Hydrobiologia*. **219**: 239-250.
- Nalewajko, C., Paul, B., Lee, K. & Shear, H. (1986) Light history, phosphorus status, and the occurrence of light stimulation or inhibition of phosphate-uptake in Lake-Superior phytoplankton and bacteria. *Canadian Journal of Fisheries and Aquatic Sciences*. **43**: 329-335.

- Nausch, M. & Nausch, K. (2004) Bacterial utilization of phosphorus pools after nitrogen and carbon amendment and its relation to alkaline phosphatase activity. *Aquatic Microbial Ecology*. **37**: 237-245.
- Neale, P. J., Davis, R. F. & Cullen, J. J. (1998) Interactive effects of ozone depletion and vertical mixing on photosynthesis of Antarctic phytoplankton. *Nature*. **392**: 585-589.
- Needham, A.E. (1957) Factors affecting nitrogen-excretion in *Carcinides maenas* (Pennant). *Physiol Comparata Et Oecol*. **4**: 209-239.
- Nithart, M., Alliot, E. & Salen-Picard, C. (1999) Production, respiration and ammonia excretion of two polychaete species in a north Norfolk saltmarsh. *Journal of the Marine Biological Association of the United Kingdom*. **79**: 1029-1037.
- Nixon, S.W., Oviatt, C.A., Garber, J. & Lee, V. (1976) Diel metabolism and nutrient dynamics in a salt-marsh embayment. *Ecology*. **57**: 740-750.
- Nöges, P. (2005) Water and nutrient mass balance of the partly meromictic temperate Lake Verevi. *Hydrobiologia*. **547**: 21-31.
- Nowlin, W. H., Davies, J. M. & Mazumder, A. (2007) Planktonic phosphorus pool sizes and cycling efficiency in coastal and interior British Columbia lakes. *Freshwater Biology*. **52**: 860-877.
- Nürnberg, G. K. (1984) The Prediction of Internal Phosphorus Load in Lakes with Anoxic Hypolimnia. *Limnology and Oceanography*. **29**:111-124.
- Nürnberg, G. K. (1988) Prediction of phosphorus release rates from total and reductant-soluble phosphorus in anoxic lake sediments. *Canadian Journal of Fisheries and Aquatic Sciences*. **45**: 453-462.
- Olin, M., Rask, M., Ruuhijarvi, J., Kurkilahti, M., Ala-Opas, P. & Ylonen, O. (2002) Fish community structure in mesotrophic and eutrophic lakes of southern Finland: the relative abundances of percids and cyprinids along a trophic gradient. *Journal of Fish Biology*. **60**: 593-612.
- Osullivan, D. W., Hanson, A. K., Miller, W. L. & Kester, D. R. (1991) Measurement of Fe(II) in surface-water of the equatorial pacific. *Limnology and Oceanography*. **36**: 1727-1741.
- Ozersky, T., Malkin, S.Y., Barton, D.R. & Hecky, R.E. (2009) Dreissenid phosphorus excretion can sustain *C. glomerata* growth along a portion of Lake Ontario shoreline. *Journal of Great Lakes Research*. **35**: 321-328.

- Park, Y.C. & Carpenter, E.J. (1987) Ammonium regeneration and biomass of macrozooplankton and Ctenophores in Great-South Bay, New-York. *Estuaries*. **10**: 316-320.
- Parmenter, R. R. & Lamarra, V. A. (1991) Nutrient Cycling in a Fresh-Water Marsh - the Decomposition of Fish and Waterfowl Carrion. *Limnology and Oceanography*. **36**: 976-987.
- Parsons, T. R., Maita, Y. & Lalli, C. M. (1984) A manual of chemical and biological methods for seawater analysis. 1st edition. Pergamon Press, Oxford.
- Paulson, L.J. (1980) Models of ammonia excretion for brook trout (*Salvelinus fontinalis*) and rainbow trout (*Salmo gairdneri*). *Canadian Journal of Fisheries and Aquatic Sciences*. **37**: 1421-1425.
- Pausz, C. & Herndl, G. J. (2002) Role of nitrogen versus phosphorus availability on the effect of UV radiation on bacterioplankton and their recovery from previous UV stress. *Aquatic Microbial Ecology*. **29**: 89-95.
- Perezruiz, T., Martinezlozano, C. & Tomas, V. (1984) Photo-oxidation of acridine and acridine yellow in the presence of iron(III) - determination of micro-amounts of iron, fluoride and phosphate. *Analyst*. **109**: 1401-1404.
- Persson, A. (1997a) Effects of fish predation and excretion on the configuration of aquatic food webs. *Oikos*. **79**:137-146.
- Persson, A. (1997b) Phosphorus release by fish in relation to external and internal load in a eutrophic lake. *Limnology and Oceanography*. **42**: 577-583.
- Peters, R.H. (1975) Phosphorus regeneration by natural populations of limnetic zooplankton. *Verhandlungen der Internationalen Vereinigung für Theoretische und Angewandte Limnologie*. **19**: 273-279.
- Peters, R. & Lean, D. (1973) The characterization of soluble phosphorus released by limnetic zooplankton. *Limnology and Oceanography*. **18**: 270-279.
- Pettersson, K. & Jansson, M. (1978) Determination of phosphatase activity in lake water. A study of methods. Sladeczek, V. (Ed.). *Internationale Vereinigung Fuer Theoretische Und Angewandte Limnologie Verhandlungen*. **20**: 1226-1230.
- Pilati, A. & Vanni, M.J. (2007) Ontogeny, diet shifts, and nutrient stoichiometry in fish. *Oikos*. **116**: 1663-1674.
- Pinto-Coelho, R.M. & Greco, M.K.B. (1999) The contribution of water hyacinth (*Eichhornia crassipes*) and zooplankton to the internal cycling of phosphorus in the eutrophic Pampulha Reservoir, Brazil. *Hydrobiologia*. **411**: 115-127.

- Porter, C.B., Krom, M.D., Robbins, M.G., Brickell, L. & Davidson, A. (1987) Ammonia excretion and total N budget for gilthead seabream (*Sparus-Aurata*) and its effect on water-quality conditions. *Aquaculture*. **66**: 287-297.
- Prins, T.C. & Smaal, A.C. (1994) The role of the blue mussel *Mytilus edulis* in the cycling of nutrients in the Oosterschelde estuary (The Netherlands). *Hydrobiologia*. **282-283**: 413-429.
- Prosch, R.M. & McLachlan, A. (1984) The regeneration of surf-zone nutrients by the sand mussel, *Donax serra* Roding. *Journal of Experimental Marine Biology and Ecology*. **80**: 221-233.
- Proulx, M., Pick, F. R., Mazumder, A., Hamilton, P. B. & Lean, D. R. S. (1996) Effects of nutrients and planktivorous fish on the phytoplankton of shallow and deep aquatic systems. *Ecology*. **77**: 1556-1572.
- Raikow, D.F., Sarnelle, O., Wilson, A.E. & Hamilton, S.K. (2004) Dominance of the noxious cyanobacterium *Microcystis aeruginosa* in low-nutrient lakes is associated with exotic zebra mussels. *Limnology and Oceanography*. **49**: 482–487.
- Ramcharan, C.W., Yan, N.D., Mcqueen, D.J., Perez-Fuentetaja, A., Demer, E. & Rusak, J.A. (2001) Complex responses of Chaoborus to changes in fish populations. *Advances in Limnology*. **56**: 81-100.
- Ramcharan, C. W., France, R. L. & McQueen, D. J. (1996) Multiple effects of planktivorous fish on algae through a pelagic trophic cascade. *Canadian Journal of Fisheries and Aquatic Sciences*. **53**: 2819-2828.
- Ramnarine, I.W., Pirie, J.M., Johnstone, A.D.F. & Smith, G.W. (1987) The influence of ration size and feeding frequency on ammonia excretion by juvenile Atlantic cod, *Gadus morhua* L. *Journal of Fish Biology*. **31**: 545-559.
- Reznick, D., Ghalambor, C. & Nunney, L. (2002) The evolution of senescence in fish. *Mechanisms of Aging and Development*. **123**: 773-789.
- Ricker, W.E. (1975) Computation and interpretation of biological statistics of fish populations. *Bulletin Fisheries Research Board of Canada*. **191**: 382.
- Schaffner, W. R., & Oglesby, R. T. (1978) Phosphorus Loadings to Lakes and Some of Their Responses .1. New Calculation of Phosphorus Loading and Its Application to 13 New-York Lakes. *Limnology and Oceanography*. **23**: 120-134.
- Schaus, M. H., Bremigan, M. T., Garvey, J. E. & Stein, R. A. (1997) Nitrogen and phosphorus excretion by detritivorous gizzard shad in a reservoir ecosystem. *Limnology and Oceanography*. **42**: 1386-1397.

- Schaus, M.H., Vanni, M.J. & Wissing, T.E. (2002) Biomass-dependent diet shifts in omnivorous gizzard shad: Implications for growth, food web, and ecosystem effects. *Transactions of the American Fisheries Society*. **131**: 40-54.
- Schindler, D.E. & Eby, L.A. (1997) Stoichiometry of fishes and their prey: Implications from nutrient recycling. *Ecology*. **78**: 1816-1831.
- Schindler, D.E., Kitchell, J.F., He, X., Carpenter, S.R., Hodgson, J.R. & Cottingham, K.L. (1993) Food web structure and phosphorus cycling in lakes. *Transactions of the American Fisheries Society*. **122**: 756-772.
- Schindler, D.E., Knapp, R.A. & Leavitt, P.R. (2001) Alteration of nutrient cycles and algal production resulting from fish introductions into mountain lakes. *Ecosystems*. **4**: 308-321.
- Schindler, D., Newbury, R. W., Beaty, K. G. & Campbell, P. (1976) Natural water and chemical budgets for a small precambrian lake basin in central Canada. *Canadian Journal of Fisheries and Aquatic Sciences*. **33**: 2526-2543.
- Schindler, D. E. & Scheuerell, M. D. (2002) Habitat coupling in lake ecosystems. *Oikos*, **98**: 177-189.
- Schindler, D.E., Scheuerell, M.D., Moore, J.W., Gende, S.M., Francis, T.B. & Palen, W.J. (2003) Pacific salmon and the ecology of coastal ecosystems. *Frontiers in Ecology and the Environment*. **1**: 31-37.
- Schneider, J. C. (1998) Fate of dead fish in a small lake. *American Midland Naturalist*. **140**: 192-196.
- Schneider, G. (1990) A comparison of carbon based ammonia excretion rates between gelatinous and nongelatinous zooplankton - implications and consequences. *Marine Biology*. **106**: 219-225.
- Schulz, E.J., Hoyer, M.V. & Canfield, D.E. (1999) An index of biotic integrity: A test with limnological and fish data from sixty Florida lakes. *Transactions of the American Fisheries Society*. **128**: 564-577.
- Scully, N. M., Tranvik, L. J. & Cooper, W. J. (2003) Photochemical effects on the interaction of enzymes and dissolved organic matter in natural waters. *Limnology and Oceanography*. **48**: 1818-1824.
- Sereda, J.M., Hudson, J.J., Taylor, W.D. & Demers, E. (2008a) Fish as sources and sinks of nutrients in lakes. *Freshwater Biology*. **53**: 278-289

- Sereda, J.M., Hudson, J.J. & McLoughlin, P.D. (2008b) General empirical models for predicting the release of nutrients by fish, with a comparison between detritivores and non-detritivores. *Freshwater Biology*. **53**: 2133-2343.
- Sereda, J.M., Hudson, J.J. & Taylor, W.D. (2009). Abiotic effect of UV on planktonic P kinetics. *Aquatic Sciences*. **71**: 127-134.
- Shelly, K., Roberts, S., Heraud, P. & Beardall, J. J. (2005) Interactions between UV-B exposure and phosphorus nutrition. I. Effects on growth, phosphate uptake, and chlorophyll fluorescence. *Journal of Phycology*. **41**: 1204-1211.
- Shostell, J. & Bukaveckas, P.A. (2004) Seasonal and interannual variation in nutrient fluxes from tributary inputs, consumer recycling and algal growth in a eutrophic river impoundment. *Aquatic Ecology*. **38**: 359-373.
- Smith, K.L. (1983) Metabolism of 2 dominant epibenthic echinoderms measured at bathyal depths in the Santa-Catalina Basin. *Marine Biology*. **72**: 249-256.
- Sommaruga, R. & Buma, A.G. J. (2000) UV-induced cell damage is species-specific among aquatic phagotrophic protists. *Journal of Eukaryotic Microbiology*. **47**: 450-455.
- Sommaruga, R., Oberleiter, A. & Psenner, R. (1996) Effect of UV radiation on the bacterivory of a heterotrophic nanoflagellate. *Applied & Environmental Microbiology*. **62**: 4395-4400.
- Sondergaard, M., Jensen, J.P. & Jeppsen, E. (2001) Retention and internal loading of phosphorus in shallow, eutrophic lakes. *The Scientific World*. **1**: 427-442.
- Soranno, P. A., Carpenter, S. R. & Lathrop, R. C. (1997) Internal phosphorus loading in Lake Mendota: response to external loads and weather. *Canadian Journal of Fisheries and Aquatic Sciences*. **54**: 1883-1893.
- Starkel, W.M. (1985) Predicting the effect of macrobenthos on the sediment water flux of metals and phosphorus. *Canadian Journal of Fisheries and Aquatic Sciences*. **42**: 95-100.
- Sterner, R.W. & Elser, J.T. (2002) Ecological stoichiometry: the biology of elements from molecules to the biosphere. Princeton University Press.
- Sterner, R.W., Elser, J.T. & Hessen, D.O. (1992) Stoichiometric relationships among producers, consumers, and nutrient cycling in pelagic ecosystems. *Biogeochemistry*. **17**: 49-67.
- Sterner, R. W. & George, N. B. (2000) Carbon, nitrogen, and phosphorus stoichiometry of cyprinid fishes. *Ecology*. **81**: 127-140.

- Tank, S. E., Xenopoulos, M. A. & Hendzel, L. L. (2005) Effect of ultraviolet radiation on alkaline phosphatase activity and planktonic phosphorus acquisition in Canadian boreal shield lakes. *Limnology and Oceanography*. **50**: 1345-1351
- Tarvainen, M., Sarvala, J. & Helminen, H. (2002) The role of phosphorus release by roach [*Rutilus rutilus* (L.)] in the water quality changes of a biomanipulated lake. *Freshwater Biology*. **47**: 2325-2336.
- Tarvainen, M., Ventela, A.M., Helminen, H. & Sarvala, J. (2005) Nutrient release and resuspension generated by ruffe (*Gymnocephalus cernuus*) and chironomids. *Freshwater Biology*. **50**: 447-458.
- Taylor, W.D. (2010). The nature of dissolved P regenerated by plankton: implications for the new ssPO₄ radiobiassay and for the determination of dissolved P. *Aquatic Sciences*. **72**: 13-20
- Taylor, W. D. & Lean, D. R. S. (1991) Phosphorus pool sizes and fluxes in the epilimnion of a mesotrophic lake. *Canadian Journal of Fisheries and Aquatic Sciences*. **48**: 1293-1301.
- Thingstad, F. T., Skjoldal, E. F. & Bohne, R. A. (1993) Phosphorus cycling and algal-bacterial competition in Sandsfjord, western Norway. *Marine Ecology Progress Series*. **99**: 239-259.
- Torres, L. & Vanni, M.J. (2007) Stoichiometry of nutrient excretion by fish: interspecific variation in a hypereutrophic lake. *Oikos*. **116**: 259-270.
- Urabe, J. (1993) N and P cycling coupled by grazers activities: food quality and nutrient release by zooplankton. *Ecology*. **74**: 2337-2350.
- Uthicke, S. (2001) Nutrient regeneration by abundant coral reef holothurians. *Journal of Experimental Marine Biology and Ecology*. **265**: 153-170.
- Vahatalo, A. V., Salonen, K., Munster, U., Jarvinen, M. & Wetzel, R. G. (2003) Photochemical transformation of allochthonous organic matter provides bioavailable nutrients in a humic lake. *Archiv Fur Hydrobiologie*. **156**: 287-314.
- Van Den Broeck, N., Moutin, T., Rodier, M. & Le Bouteiller, A. (2004) Seasonal variations of phosphate availability in the SW Pacific Ocean near New Caledonia. *Marine Ecology-Progress Series*. **268**: 1-12.
- Vanderploeg, H.A., Liebig, J.R., Carmichael, W.W., Agy, M.A., Johengen, T.H., Fahnenstiel, G.L. & Nalepa, T.F. (2001) Zebra mussel (*Dreissena polymorpha*) selective filtration promoted toxic *Microcystis* blooms in Saginaw Bay (Lake Huron) and Lake Erie. *Canadian Journal of Fisheries and Aquatic Sciences*. **58**: 1208–1221.

- Vander Zanden, M. J. & Rasmussen, J. B. (1999) Primary consumer delta C-13 and delta N-15 and the trophic position of aquatic consumers. *Ecology*. **80**: 1395-1404.
- Vander Zanden, M.J. & Vadeboncoeur, Y. (2002) Fishes as integrators of benthic and pelagic food webs in lakes. *Ecology*. **83**: 2152-2161.
- Vanni, M.J. (2002) Nutrient cycling by animals in freshwater ecosystems. *Annual Review of Ecology and Systematics*. **33**: 341-370.
- Vanni, M.J., Bowling, A.M., Dickman, E.M., Hale, R.S., Higgins, K.A., Horgan, M.J., Knoll, L.B., Renwick, W.H. & Stein, R.A. (2006) Nutrient cycling by fish supports relatively more primary production as lake productivity increases. *Ecology*. **87**: 1696-1709.
- Vanni, M. J. & Findlay, D. L. (1990) Trophic cascades and phytoplankton community structure. *Ecology*. **71**: 921-937.
- Vanni, M.J., Flecker, A.S., Hood, J.M. & Headworth, J.L. (2002) Stoichiometry of nutrient recycling by vertebrates in a tropical stream: linking species identity and ecosystem processes. *Ecology Letters*. **5**: 285-293.
- Vaughn, C.C., Mather, C.M., Pyron, M., Mehlhop, P. & Miller, E.K. (1996) The current and historical mussel fauna of the Kiamichi River, Oklahoma. *Southwestern Naturalist*. **41**: 325-328.
- Verant, M.L., Konsti, M.L., Zimmer, K.D. & Deans, C.A. (2007) Factors influencing nitrogen and phosphorus excretion rates of fish in a shallow lake. *Freshwater Biology*. **52**: 1968-1981.
- Verdon, R. & Magnin, E. (1977) Dynamics of the population of whiter suckers *Catostomus commersonii commersonii* (Lacépède) in lac Croche in the Laurentides, Québec. *Le Naturaliste Canadien*. **104**: 196-205.
- Villafane, V. E., Helbling, E. W., Holm-Hansen O. & Chalker, B. E. (1995) Acclimatization of Antarctic natural phytoplankton assemblages when exposed to solar ultraviolet radiation. *Journal of Plankton Research*. **17**: 2295-2306.
- Vinebrooke, R. D. & Leavitt, P. R. (1998) Direct and interactive effects of allochthonous dissolved organic matter, inorganic nutrients, and ultraviolet radiation on an alpine littoral food web. *Limnology and Oceanography*. **43**: 1065-1081.
- Voelker, B. M., Morel, F. M. M. & Sulzberger, B. (1997) Iron redox cycling in surface waters: Effects of humic substances and light. *Environmental Science and Technology*. **31**: 1004-1011.

- Walker, W. W. & Havens, K. E. (2003) Development and application of a phosphorus balance model for Lake Istokpoga, Florida. *Lake and Reservoir Management*. **19**: 79-91.
- Warton, D. I., Wright, I. J., Falster, D. S. & Westoby, M. (2006) Bivariate line-fitting methods for allometry. *Biological Reviews*. **81**: 1-15.
- Welsh, P. G., Parrott, J. L., Dixon, D. G., Hodson, P. V., Spry, D. J. & Mierle, G. (1996) Estimating acute copper toxicity to larval fathead minnow (*Pimephales Promelas*) in soft water from measurements of dissolved organic carbon, calcium, and pH. *Canadian Journal of Fisheries and Aquatic Sciences*. **53**: 1263-1271.
- Wen, Y.H. & Peters, R.H. (1994) Empirical models of phosphorus and nitrogen excretion rates by zooplankton. *Limnology and Oceanography*. **39**: 1669-1679.
- Wetzel, R. G., Hatcher, P. G. & Bianchi, T. S. (1995) Natural photolysis by ultraviolet irradiance of recalcitrant dissolved organic matter to simple substrates for rapid bacterial metabolism. *Limnology and Oceanography*. **40**: 1369-1380.
- Wetzel, R. G. & Likens, G. E. (1991) *Limnological Analyses*. 2nd edition. Springer-Verlag, New York.
- White, E. M., Vaughan, P. P. & Zepp, R. G. (2003) Role of the photo-Fenton reaction in the production of hydroxyl radicals and photobleaching of colored dissolved organic matter in a coastal river of the southeastern United States. *Aquatic Sciences*. **65**: 402-414.
- Wilhelm, F.M., Hudson, J.J., & Schindler, D.W. (1999) Contribution of Gammarus lacustris to phosphorus recycling in a fishless alpine lake. *Canadian Journal of Fisheries and Aquatic Sciences*. **56**: 1679-1686.
- Wilson, A.E. & Sarnelle, O. (2002) Relationship between zebra mussel biomass and total phosphorus in European and North American lakes. *Archive Für Hydrobiologie*. **153**: 339-351.
- Winemiller, K. O. (1989) Ontogenetic diet shifts and resource partitioning among piscivorous fishes in the Venezuelan Llanos. *Environmental Biology of Fishes*. **26**: 177-199.
- Wurtsbaugh, W. A. (2007) Nutrient cycling and transport by fish and terrestrial insect nutrient subsidies to lakes. *Limnology and Oceanography*. **52**: 2715-2718.
- Xenopoulos, M. A. & Frost, P. C. (2003) UV radiation, phosphorus, and their combined effects on the taxonomic composition of phytoplankton in a boreal lake. *Journal of Phycology*. **39**: 291-302.

- Xenopoulos, M. A., Frost, P. C. & Elser, J. J. (2002) Joint effects of UV radiation and phosphorus supply on algal growth rate and elemental composition. *Ecology*. **83**: 423-435.
- Yan, N.D., Perez-Fuentetaja, A., Ramcharan, C.W., Mcqueen, D.J., Demers, E. & Rusak, J.A. (2001) Changes in the crustacean zooplankton communities of Mouse and Ranger Lakes. *Advances in Limnology*. **56**: 127-150.
- Yager, T.K. & Summerfelt, R.C. (1993) Effects of fish size and feeding frequency on metabolism of juvenile walleye. *Aquacultural Engineering*. **12**: 19-36.
- Zafiriou, O. C. & True, M. B. (1979) Nitrate photolysis in seawater by sunlight. *Marine Chemistry*. **8**: 33-42.
- Zakes, Z. & Karpinski, A. (1999) Influence of water temperature on oxygen consumption and ammonia excretion of juvenile pikeperch, *Stizostedion lucioperca* (L.) reared in a recirculating system. *Aquaculture Research*. **30**: 109-114.
- Zar, J.H. (1999) *Biostatistical analysis*, Prentice Hall, Upper Saddle River, N.J.
- Zellner, R., Exner, M. & Herrmann, H. (1990) Absolute OH quantum yields in the laser photolysis of nitrate, nitrite and dissolved H₂O₂ at 308 and 351 nm in the temperature-range 278-353 K. *Journal of Atmospheric Chemistry*. **10**: 411-425.
- Zepp, R. G., Faust, B. C. & Hoigne, J. (1992) Hydroxyl radical formation in aqueous reactions (pH 3-8) of iron(II) with hydrogen-peroxide - the photo-fenton reaction. *Environmental Science and Technology*. **26**: 313-319.
- Zhou, Y. Y., 1996. UV-sensitive P compounds: Release mechanism, seasonal fluctuation and inhibitory effects on alkaline phosphatase activity in a shallow Chinese freshwater lake (Donghu Lake). *Hydrobiologia*. **335**: 55-62.
- Zimmer, K.D., Herwig, B.R. & Laurich, L.M. (2006) Nutrient excretion by fish in wetland ecosystems and its potential to support algal production. *Limnology and Oceanography*. **51**: 197-207.

Appendix 3.1. Directly measured nutrient release rates (N and P) for model development were obtained from the literature. Models were developed for meso- and macrozooplankton, mussels and benthic macroinvertebrates (other than mollusca).

Zooplankton

- Andersen, V. (1989) Phosphate excretion rate of *Salpa fusiformis* Cuvier (Tunicata, Thaliacea). *Hydrobiologia*. **171**: 91-97.
- Atkinson, A. & Whitehouse, M.J. (2001) Ammonium regeneration by Antarctic mesozooplankton: an allometric approach. *Marine Biology*. **139**: 301-311.
- Bamstedt, U. & Tande, K.S. (1985) Respiration and excretion rates of *Calanus glacialis* in Arctic waters of the Barents Sea. *Marine Biology*. **87**: 259-266.
- Burkhardt, S. & Lehman, J.T. (1994) Prey consumption and predatory effects of an invertebrate predator (*Bythotrephes*): Cladocera, Cercopagidae) based on phosphorus budgets. *Limnology and Oceanography*. **39**: 1007-1019.
- Ejsmont-Karabin, J. (1983) Ammonia nitrogen and inorganic phosphorus excretion by the planktonic rotifers. *Hydrobiologia*. **104**: 231-236.
- Gaudy, R. & Boucher, J. (1983) Relation between respiration, excretion (ammonia and inorganic phosphorus) and activity of amylase and trypsin in different species of pelagic copepods from an Indian-Ocean equatorial area. *Marine Biology*. **75**: 37-45.
- Gorsky, G., Palazzoli, I. & Fenaux, R. (1987) Influence of temperature-changes on oxygen-uptake and ammonia and phosphate excretion, in relation to body size and weight, in *Oikopleura dioica* (Appendicularia). *Marine Biolog.* **94**: 191-201.

- Hirche, H.J. (1983) Excretion and Respiration of the Antarctic Krill *Euphausia superba*. *Polar Biology*. **1**: 205-209.
- Ikeda, T. & Kirkwood, R. (1989) Metabolism and elemental composition of a giant Chaetognath *Sagitta gazellae* from the Southern-Ocean. *Marine Biology*. **100**: 261-267.
- Ikeda, T. & Mitchell, A.W. (1982) Oxygen-uptake, ammonia excretion and phosphate excretion by krill and other Antarctic zooplankton in relation to their body size and chemical-composition. *Marine Biology*. **71**: 283-298
- Jawed, M. (1973) Ammonia excretion by zooplankton and its significance to primary productivity during summer. *Marine Biology*. **23**: 115-120.
- Biggs, D.C. (1982) Zooplankton excretion and NH₄⁺ cycling in near-surface waters of the southern-ocean.1. Ross Sea, Austral Summer 1977-1978. *Polar Biology*. **1**: 55-67
- Pinto-Coelho, R.M., Demoura, R.T. & Moreira, A. (1997) Zooplankton and bacteria contribution to phosphorus and nitrogen internal cycling in a tropical and eutrophic reservoir: Pampulha lake, Brazil. *Internationale Revue Der Gesamten Hydrobiologie*. **82**: 185-200.
-

Mussels

- Aldridge, D.W., Payne, B.S. & Miller, A.C. (1995) Oxygen consumption, nitrogenous excretion, and filtration rates of *Dreissena polymorpha* at acclimation temperatures between 20 and 32 degree C. *Canadian Journal of Fisheries and*

- Aquatic Sciences*. **52**: 1761-1767.
- Bayne, B.L. & Scullard, C. (1977) Rates of nitrogen-excretion by species of *Mytilus* (Bivalvia – Mollusca). *Journal of the Marine Biological Association of the United Kingdom*. **57**: 355-369.
- Clarke, A., Protherothomas, E. & Whitehouse, M.J. (1994) Nitrogen-excretion in the Antarctic limpet *Nacella concinna* (Strebel, 1908). *Journal of Molluscan Studies*. **60**: 141-147.
- Conroy, J.D., Edwards, W.J., Pontius, R.A., Kane, D.D., Zhang, H.Y., Shea, J.F., Richey, J.N. & Culver, D.A. (2005) Soluble nitrogen and phosphorus excretion of exotic freshwater mussels (*Dreissena* spp.): potential impacts for nutrient remineralisation in western Lake Erie. *Freshwater Biology*. **50**: 1146-1162.
- Davis, W.R., Christian, A.D., Berg, D.J. (1999) Nitrogen and phosphorus cycling by freshwater mussels (Bivalvia: Unionidae) in a headwater stream ecosystem. *Proceedings of the First Freshwater Mollusk Conservation Society Symposium*. 141-151.
- Follum, O.A. & Gray, J.S. (1987) Nitrogenous excretion by the sediment-living bivalve *Nucula tenuis* from the Oslofjord, Norway. *Marine Biology*. **96**: 355-358.
- James, M.R., Weatherhead, M.A. & Ross, A.H. (2001) Size-specific clearance, excretion, and respiration rates, and phytoplankton selectivity for the mussel *Perna canaliculus* at low levels of natural food. *New Zealand Journal of Marine and Freshwater Research*. **35**: 73-86.
- James, W.F., Barko, J.W., Davis, M., Eakin, H.L., Rogala, J.T. & Miller, A.C. (2000) Filtration and excretion by zebra mussels: Implications for water quality impacts

- in Lake Pepin, upper Mississippi River. *Journal of Freshwater Ecology*. **15**: 429-437.
- Jordan, T.E. & Valiela, I. (1982) A nitrogen budget of the ribbed mussel, *Geukensia demissa*, and its significance in nitrogen flow in a New-England salt-marsh. *Limnology and Oceanography*. **27**: 75-90.
- Kiibus, M. & Kautsky, N. (1996) Respiration, nutrient excretion and filtration rate of tropical freshwater mussels and their contribution to production and energy flow in Lake Kariba, Zimbabwe. *Hydrobiologia*. **331**: 25-32.
- Lauritsen, D.D. & Mozley, S.C. (1989) Nutrient excretion by the Asiatic clam *Corbicula fluminea*. *Journal of the North American Benthological Society*. **8**: 134-139.
- Martin, S., Thouzeau, G., Chauvaud, L., Jean, F., Guerin, L. & Clavier, J. (2006) Respiration, calcification, and excretion of the invasive slipper limpet, *Crepidula fornicata* L.: Implications for carbon, carbonate, and nitrogen fluxes in affected areas. *Limnology and Oceanography*. **51**: 1996-2007.
- Mellina, E., Rasmussen, J.B. & Mills, E.L. (1995) Impact of zebra mussel (*Dreissena polymorpha*) on phosphorus cycling and chlorophyll in lakes. *Canadian Journal of Fisheries and Aquatic Sciences*. **52**: 2553-2573.
- Nalepa, T.F., Gardner, W.S. & Malczyk, J.M. (1991) Phosphorus cycling by mussels (Unionidae, Bivalvia) in Lake St-Clair. *Hydrobiologia*. **219**: 239-250.
- Prosch, R.M. & McLachlan, A. (1984) The regeneration of surf-zone nutrients by the sand mussel, *Donax serra* Roding. *Journal of Experimental Marine Biology and Ecology*. **80**: 221-233.
- Srna, R.F. & Baggaley, A. (1976) Rate of excretion of ammonia by hard clam

- Mercenaria mercenaria* and American oyster *Crassostrea virginica*. *Marine Biology*. **36**: 251-258.
- Vaughn, C.C., Gido, K.B. & Spooner, D.E. (2004) Ecosystem processes performed by unionid mussels in stream mesocosms: species roles and effects of abundance. *Hydrobiologia*. **527**: 35-47.
- Vink, S. & Atkinson, M.J. (1985) High dissolved C-P excretion ratios for large benthic marine-invertebrates. *Marine Ecology-Progress Series*. **21**: 191-195.
- Yamamuro, M. & Koike, I. (1993) Nitrogen-metabolism of the filter-feeding bivalve *Corbicula japonica* and its significance in primary production of a brackish lake in Japan. *Limnology and Oceanography*. **38**: 997-1007.
-

Benthic Macroinvertebrates

- Fukuhara, H. & Yasuda, K. (1989) Ammonium excretion by some fresh-water zoobenthos from a eutrophic lake. *Hydrobiologia*. **173**: 1-8.
- Gardner, W.S., Briones, E.E., Kaegi, E.C. & Rowe, G.T. (1993) Ammonium excretion by benthic invertebrates and sediment-water nitrogen flux in the Gulf-of-Mexico near the Mississippi River outflow. *Estuaries*. **16**: 799-808.
- Gray, J.S. (1985) Nitrogenous excretion by meiofauna from coral-reef sediments - Mecor-5. *Marine Biology*. **89**: 31-35.
- Grimm, N.B. (1988) Role of macroinvertebrates in nitrogen dynamics of a desert stream. *Ecology*. **69**: 1884-1893.
- Henry, R. & Santos, C.M. (2008) The importance of excretion by Chironomus larvae on

- the internal loads of nitrogen and phosphorus in a small eutrophic urban reservoir. *Brazilian Journal of Biology*. **68**: 349-357.
- Kouassi, E., Pagano, M., Saint-Jean, L. & Sorbe, J.C. (2006) Diel vertical migrations and feeding behavior of the mysid *Rhopalophthalmus africana* (Crustacea : Mysidacea) in a tropical lagoon (Ebrie, Cote d'Ivoire). *Estuarine Coastal and Shelf Science*. **67**: 355-368.
- Nelson, S.G., Simmons, M.A. & Knight, A.W. (1979) Ammonia excretion by the benthic estuarine shrimp *Crangon franciscorum* (Crustacea, Crangonidae) in relation to diet. *Marine Biology*. **54**: 25-31.
- Tatrai, I. (1982) Oxygen-consumption and ammonia excretion of herbivorous Chironomid larvae in Lake Balaton. *Hydrobiologia*. **96**: 129-135.
- Vink, S. & Atkinson, M.J. (1985) High dissolved C-P excretion ratios for large benthic marine-invertebrates. *Marine Ecology-Progress Series*. **21**: 191-195.
- Wilhelm, F.M., Hudson, J.J. & Schindler, D.W. (1999) Contribution of *Gammarus lacustris* to phosphorus recycling in a fishless alpine lake. *Canadian Journal of Fisheries and Aquatic Sciences*. **56**: 1679-1686.
-

Publications and Conference Presentations

Articles Published or Accepted in Peer-Reviewed Journals

Sereda Jeff M., David M. Vandergucht, Jeff J. Hudson (2011) Disruption of Planktonic Phosphorus Cycling by Ultraviolet Radiation. *Hydrobiologia*. **665**:205–217. (JIF: 1.81; 27/88 Marine & Freshwater Biology)

Sereda Jeff M., Jeff J. Hudson (2011) Empirical models for predicting the release of nutrients (N and P) by aquatic metazoans: taxonomic differences in rates and element ratios. *Freshwater Biology*. **56**: 250-263. (JIF: 3.29; 8/88 Marine & Freshwater Biology)

Sereda Jeff, Mathew Bogard, Jeff Hudson, Devin Helps, Tarik Dessouki (2011) Climate warming and the onset of salinization: rapid changes in the limnology of two northern plains lakes. *Limnologia*. **41**: 1-9. (JIF: 1.58; 7/18 Limnology)

Jan Zhang, Jeff Hudson, Richard Neal, **Jeff Sereda**, Thomas Clair, Michael Turner, Dean Jeffries, Peter Dillon, Lewis Molot, Keith Somers, and Ray Hesslein (2010) Long-term patterns of dissolved organic carbon in lakes across eastern Canada: evidence of a pronounced climate effect. *Limnology and Oceanography*. **55**: 30-42 (JIF: 4.09; 1/18 Limnology)

Sereda, Jeff M., Jeff J. Hudson (2010) A comparative estimate of P fluxes in lakes: A comment on “Fish decomposition in boreal lakes and biogeochemical implications” by Chidami and Amyot (2008) *Limnology and Oceanography* **55**: 463-465. (JIF: 4.09; 1/18 Limnology)

Sereda, Jeff M., Jeff J. Hudson, Philip D. McLoughlin (2008) General empirical models for predicting the release of nutrients by fish with a comparison between detritivores and non-detritivores. *Freshwater Biology*. **53**: 2133-2144. (JIF: 3.29; 8/88 Marine & Freshwater Biology)

Sereda, Jeff M., Jeff J. Hudson, William D. Taylor, Eric Demers (2008) Fish as sources and sinks of nutrients in lakes. *Freshwater Biology*. **52**: 278-289. (JIF: 3.29; 8/88 Marine & Freshwater Biology)

Invited Contributions for Publication in Peer-Reviewed Journals

Sereda, Jeff M., Jeff J. Hudson, William D. Taylor (2009) Abiotic effects of UV on planktonic phosphorus kinetics. *Aquatic Sciences*. **71**: 127-134. (JIF: 2.71; 3/18 Limnology)

Contributed Presentations at Conferences (* denotes presenting author)

Sereda Jeff M.*, Jeff J. Hudson, John-Mark Davies (2011) The Contribution of Point and Diffuse Sources of Nutrients to the Eutrophication of Lake Diefenbaker: A Sensitivity Analysis. Prairie University Biological Symposium, Saskatoon, SK

Hoemsen Brittney*, **Jeff M. Sereda**, Jeff J. Hudson, John-Mark Davies (2011) Spatial Heterogeneity of Eutrophication in Lake Diefenbaker: Causes and Consequences. Prairie University Biological Symposium, Saskatoon, SK

Vandergucht David M.* , **Jeff M. Sereda**, Jeff J. Hudson (2011) Zooplankton and phosphorus deficiency in lakes - the role of ecological stoichiometry. Prairie University Biological Symposium, Saskatoon, SK

Sereda Jeff M. *, Jeff J. Hudson (2011) Empirical models for predicting the release of nutrients (N and P) by aquatic metazoans: taxonomic differences in rates and element ratios. Society of Canadian Limnologists Annual Meeting, Toronto, ON

Vandergucht, David M. *, **Jeff M. Sereda**, Jeff J. Hudson (2011) Relationship between zooplankton community structure and phosphate turnover time in lake foodwebs. Society of Canadian Limnologists Annual Meeting, Toronto, ON

Hunter, Kristine, **Sereda Jeff M.**, David M. Vandergucht, Jeff J. Hudson* (2011) Photochemical mineralization of dissolved organic nitrogen to ammonia in prairie lakes. Society of Canadian Limnologists Annual Meeting, Toronto, ON

Sereda Jeff M. *, David M. Vandergucht, Jeff J. Hudson (2010) Ultraviolet radiation modulates phosphate partitioning between plankton size fractions. American Society of Limnology and Oceanography Annual Meeting, Santa Fe, NM

Sereda Jeff M. *, David M. Vandergucht, Jeff J. Hudson (2010) Photoinhibition of phosphate uptake in UVR exposed plankton assemblages: rate of recovery and influence of cell size. Society of Canadian Limnologists Annual Meeting, Winnipeg, MB

Vandergucht, David M. *, **Jeff M. Sereda**, Jeff J. Hudson (2010) Phosphorus deficiency indicators in lakes. Society of Canadian Limnologists Annual Meeting, Winnipeg, MB

Sereda Jeff M.*, David M. Vandergucht, Jeff J. Hudson (2009) Effects of ultraviolet radiation on phosphorus kinetics within plankton assemblages. Aquatic Sciences Annual Meeting, Nice, FR

Vandergucht, David M.* , **Jeff M. Sereda**, Jeff J. Hudson (2009) A comparison of techniques for determining P-limitation in lakes. Society of Canadian Limnologists Annual Meeting, Ottawa, ON

Sereda, Jeff M. *, Jeff J. Hudson, William D. Taylor (2008) Effects of ultraviolet radiation on phosphorus kinetics in lakes. American Society of Limnology and Oceanography Annual Meeting, St. Johns, NFLD

Sereda, Jeff M. *, Jeff J. Hudson, Phillip D. McLoughlin (2008) General empirical models for predicting the release of nutrients by fish with a comparison between detritivores and non-detritivores. Society of Canadian Limnologists Annual Meeting, Halifax, NS

Sereda, Jeff M. *, Jeff J. Hudson, Philip D. McLoughlin (2007) Empirical models for predicting the release of nutrients by fish. Canadian Water Resources Association Annual Meeting, Saskatoon, SK

Sereda, Jeff M. *, Jeff J. Hudson, William D. Taylor, Eric Demers (2007) The significance of nutrient release by fish in Mouse and Ranger lakes. North American Lake Management Society Annual Meeting, Indianapolis, IN

Sereda, Jeff M. *, Jeff J. Hudson, William D. Taylor, Eric Demers (2006) The significance of nutrient release by fish in Mouse and Ranger lakes. Society of Canadian Limnologists Annual Meeting, Calgary, AB